Renewable and Sustainable Energy Reviews 16 (2012) 143–169

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Review of biodiesel composition, properties, and specifications

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ARTICLE INFO

Article history:
Received 27 April 2011
Accepted 5 July 2011
Available online 20 October 2011

Keywords:
Biodiesel
Biodiesel composition
Biodiesel properties
Biodiesel specifications
FAME

ABSTRACT

Biodiesel is a renewable transportation fuel consisting of fatty acid methyl esters (FAME), generally produced by transesterification of vegetable oils and animal fats. In this review, the fatty acid (FA) profiles of 12 common biodiesel feedstocks were summarized. Considerable compositional variability exists across the range of feedstocks. For example, coconut, palm and tallow contain high amounts of saturated FA; while corn, rapeseed, safflower, soy, and sunflower are dominated by unsaturated FA. Much less information is available regarding the FA profiles of algal lipids that could serve as biodiesel feedstocks. However, some algal species contain considerably higher levels of poly-unsaturated FA than is typically found in vegetable oils.

Differences in chemical and physical properties among biodiesel fuels can be explained largely by the fuels' FA profiles. Two features that are especially influential are the size distribution and the degree of unsaturation within the FA structures. For the 12 biodiesel types reviewed here, it was shown that several fuel properties – including viscosity, specific gravity, cetane number, iodine value, and low temperature performance metrics – are highly correlated with the average unsaturation of the FAME profiles. Due to opposing effects of certain FAME structural features, it is not possible to define a single composition that is optimum with respect to all important fuel properties. However, to ensure satisfactory in-use performance with respect to low temperature operability and oxidative stability, biodiesel should contain relatively low concentrations of both long-chain saturated FAME and poly-unsaturated FAME.

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1364-0321/$ – see front matter
doi:10.1016/j.rser.2011.07.143

1. Introduction

1.1. Background

Interest in biodiesel is continuing to increase in the U.S. and throughout the world. This is motivated primarily by: (1) concerns about greenhouse gas (GHG) emissions and global climate change, (2) a desire for renewable/sustainable energy sources, and (3) an interest in developing domestic and more secure fuel supplies. In recent years, several countries (and states) have embarked on legislative and/or regulatory pathways that encourage increased use of biodiesel fuel – using both incentives and prescriptive volumetric requirements. For example, in the U.S., the Energy Independence and Security Act (EISA) of 2007 established a 0.5 billion gallon/year (bg/y) requirement for biomass-based diesel fuel in 2009, with this amount increasing to 1.0 bg/y by 2012 [1].

With the biodiesel landscape being in a state of rapid flux, the Coordinating Research Council (CRC) recently sponsored Project AVFL-17 to define the state-of-knowledge regarding biodistillates as blendstocks for transportation fuels. Utilizing an extensive literature review, this project investigated numerous topic areas, including policy drivers, fuel volumes and feedstocks, production technologies, fuel properties and specifications, in-use handling and performance, emissions impacts, and life-cycle analyses. Results of this literature review are available in a project final report [2] and in a series of papers derived from this report [3–5].

More recently, CRC sponsored an updated review of the biodistillate literature. In this case, the focus was on biodiesel – as opposed to the broader category of biodistillate fuels – and was limited to fewer specific topic areas. The complete final report from this updated study is available from the CRC website [6]. The subject of this paper is limited to a review of biodiesel compositions and properties, and the relationships between composition and properties.

1.2. Definitions

Biodiesel is defined by ASTM as "a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100" [7]. Congress has adopted a similar definition for "biomass-based diesel," with the additional requirement that the fuel have life-cycle greenhouse gas (GHG) emissions that are at least 50% less than baseline life-cycle GHG [1]. The vegetable- and animal-derived feedstocks used to produce biodiesel are known as triacylglycerides (TAGs), or more simply, triglycerides. Biodiesel is produced by a chemical process known as transesterification, by which the triglycerides are reacted with alcohols, in the presence of a catalyst, to produce fatty acid alkyl esters. A byproduct of transesterification is glycerine, also known as glycerol. Since the most common alcohol used to produce biodiesel is methanol, another name for biodiesel is fatty acid methyl esters (FAME). Unless otherwise indicated, the term "biodiesel" refers to neat material – i.e. 100% FAME, often designated as B100. Lower concentrations, such as B20, are properly referred to as "biodiesel blends," not biodiesel itself.

Renewable diesel fuel (also known as Green Diesel) is produced by catalytic hydroprocessing of the same triglyceride feedstocks used to produce biodiesel [8,9]. In this process, an alcohol is not required, the products are hydrocarbons rather than fatty acid alkyl esters, and no glycerol byproduct is formed. The general term "biodistillate" is used to refer to both biodiesel and renewable diesel.

Terminology regarding "1st Generation" and "2nd Generation" biofuels are in popular usage, but have no legal or regulatory meaning. Generally, the term "1st Generation" refers to biofuels produced from commonly available, edible feedstocks using well-established conversion technologies. Most biofuels in use today are classified as 1st Generation. This includes ethanol produced via fermentation of sugars (from corn, sugar cane, sorghum, etc.) and biodiesel produced via transesterification of triglycerides (from vegetable oils and animal fats). The term "2nd Generation" can refer to biofuels produced from either advanced, non-food feedstocks, or produced via advanced processing technology (or both). Examples of advanced feedstocks include lignocellulose and non-edible triglycerides (such as jatropha and algae). Examples of advanced processing technology include catalytic hydroprocessing of triglycerides to produce renewable diesel, and thermal conversion (gasification and pyrolysis) of lignocellulose. Because of their imprecise and variable meanings, this paper avoids use of the terms 1st Generation and 2nd Generation (and related terms).

2. Biodiesel composition

Biodiesel fuel can be produced by transesterification of virtually any triglyceride feedstock. This includes oil-bearing crops, animal fats, and algal lipids. The literature contains hundreds of references of biodiesel production from a wide variety of feedstocks. At present, however, the dominant feedstocks are soybean oil in the U.S., rapeseed oil in Europe, and palm oil in southeast Asia [2,10]. Animal fats (especially beef tallow) and used cooking oil (also called yellow grease) represent significant niche markets

Table 1
Potential biodiesel yield from triglyceride feedstocks.

Source	Potential annual yield, gallons/acre	Source of info (reference nos.)
Corn	18–20	[129–131]
Cotton	35–45	[107,130,131]
Soybean	40–55	[10,107,129–133]
Mustard	60–140	[10,134]
Camelina	60–65	[134,135]
Safflower	80–85	[129,134,135]
Sunflower	75–105	[107,130,133,134]
Canola	110–145	[10,107,129,130,134]
Rapeseed	110–130	[107,133–136]
Jatropha	140–200	[10,130,133–135,137]
Coconut	250–300	[107,134,135]
Palm oil	400–650	[10,107,129,130,133–135]
Algae	>5000[a]	[10,23,129,134,135]

[a] Figure for algae is based upon extrapolations from small scale operations, and is quite speculative.

for biodiesel in many locations. Other vegetable oils having real or potential commercial interest as biodiesel feedstocks include camelina, canola, coconut, corn, jatropha, safflower, and sunflower.

In addition, there is great interest in developing and utilizing algal lipids as biodiesel feedstocks. Of all photosynthetic organisms, microalgae are the most productive users of CO_2, and can fix larger amounts of CO_2 per land area than other plants [11]. Table 1 summarizes potential yields of biodiesel that could be produced from various triglyceride feedstocks. While many of these values are rather speculative, it appears that algae has the potential to produce significantly larger annual volumes of biodiesel per acre as compared to other sources.

Although biodiesel fuel produced from transesterification of triglycerides contains numerous individual FAME species, a particular fuel is generally dominated by only a few species. A list of fatty acids (FA) most commonly seen in biodiesel is provided in Table 2. A simple FA naming convention is also shown in this table. This convention consists of two numbers, separated by a colon symbol. The first number refers to the number of carbon atoms in the FA chain; the second number refers to the number of carbon–carbon double bonds in the FA chain.

Of the 13 species shown in Table 2, 5 typically dominate the composition of FAME derived from vegetable oils and animal fats: palmitic acid (16:0), stearic acid (18:0), oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3). Some algal-derived lipids are dominated by these same fatty acid groups, while other algae are more diverse in their composition, containing significant amounts of several other FA groups. Biodiesel (FAME) produced from transesterification of triglycerides, regardless of their source, is composed nearly exclusively of even-numbered FA chains. In contrast, renewable diesel produced from the same feedstocks contains substantial amounts of odd-numbered FA chains, since one carbon is removed during the hydroprocessing step used to manufacture renewable diesel.

2.1. Compositional profiles of biodiesel from fats and oils

For the purposes of this review, 12 common fat and oil materials were considered as biodiesel feedstocks. These 12 materials are shown in Table 3, which provides fatty acid (FA) compositional information for each one. Three of these 12 materials are predicted by EPA to provide most of the total volume of biodiesel needed to satisfy the RFS2 requirements for biomass-based diesel by the year 2022: soy oil (660 mg/y), corn oil (680 mg/y), and yellow grease (230 mg/y), with the remainder predicted to come from algae (100 mg/y) [12].

The compositional data shown in Table 3 were obtained by reviewing and summarizing numerous literature sources. Many literature references cite compositional data derived from other sources. Whenever possible, original sources were obtained and reviewed. The data in Table 3 include FA compositions of both triglyceride feedstocks and (FAME) produced from these feedstocks. (It is generally assumed that FA compositional profiles remain unchanged during conversion of the feedstocks to fuels via transesterification.)

Table 3 also indicates the number of literature references used to obtain the average compositional profiles. These varied from 6 sources (for camelina) to 39 sources (for soy). The literature sources themselves are listed in Table 4. While actual compositions do vary somewhat based upon growing conditions and locations, much of the variability reported for these compositional profiles probably results from use of different analytical methods – and different skill levels in applying these methods.

Very few reports in the literature document carefully controlled studies that investigate the impacts of growth conditions (water, nutrients, temperature, etc.) upon the fatty acid profiles of vegetable oils. One controlled field experiment with Jatropha demonstrated that the profile did not change dramatically with growth conditions, although the total amount of fatty acids did [13]. Another study, involving sunflower, inferred more significant changes in FA profile, based upon variations in iodine values, which correlate with degree of unsaturation [14].

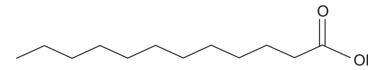
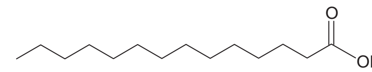
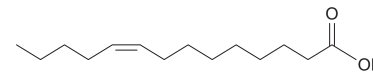
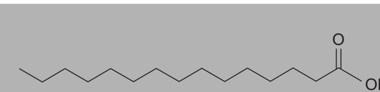
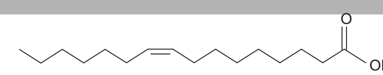
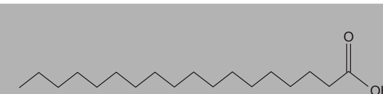
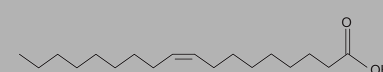
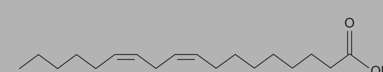
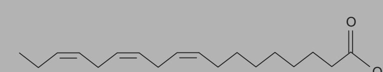
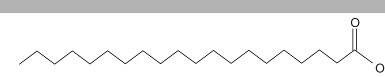
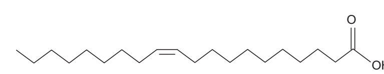
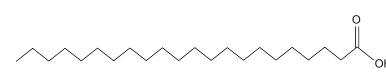
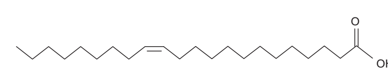
In this review, no *a priori* judgments were made regarding the validity of reported compositional data. All values were initially accepted, and weighted equally to compute a mean compositional result (wt.%) for each species. The distribution of values reported for an individual species (from a given feedstock) was then inspected, and values far from the mean (typically > 2 standard deviations) were identified. These “outliers” were first investigated by re-inspecting the original literature source and correcting data entry errors. In a few cases, even though no obvious errors could be identified, outliers were eliminated when calculating means and standard deviations.

The average profiles summarized in Table 3 have been adjusted by eliminating outliers. Empty cells represent FA species that were not reported in any reference that was reviewed. Cases which show a mean value but no standard deviation indicate that only one reference was found for this FA. The reader will note that the sum of species in these average profiles does not equal 100%. In part, this is due to rounding issues. However, it is also a consequence of the way in which mean concentration values were determined. The mean values were obtained by averaging only reported non-zero values. In some instances, only a few references reported values for a minor FA in a given profile, while other references reported nothing. In such cases, averaging only the positive values has the effect of over estimating the concentration of these minor species.

Average compositional profiles of biodiesel from four common feedstocks (palm, rapeseed, soy, and yellow grease) are shown graphically in Fig. 1. (Profiles of all 12 feedstocks investigated are included in Fig. S-1 of the Supplemental Information.) These depictions provide useful insights into differences among the various biodiesel types. For example, most of the 12 compositions are dominated by C_{18} compounds, while a few have substantial amounts of lighter compounds; especially C_{12} for coconut and C_{16} for palm.

Of the fuels dominated by C_{18}, the relative amounts of saturated (18:0), mono-unsaturated (18:1) and di-unsaturated (18:2) compounds varies considerably. Rapeseed and canola (a close relative of rapeseed) contain mostly 18:1; corn, safflower, soy, and sunflower contain mostly 18:2; jatropha, and yellow grease have more nearly equal amounts of 18:1 and 18:2. Of the 12 feedstocks investigated, camelina contains the highest level of 18:3. Of interest is the reported presence of lignoceric acid (24:0) in jatropha-derived FAME. The mean concentration of 2.6% comes from just two literature values – out of 20 total sources. Thus, this value may

Table 2
Typical fatty acid (FA) groups in biodiesel (shaded compounds are most common).

Common Name	Formal Name	CAS. No.	Abbreviation	Molecular Formula	Molecular Weight	Molecular Structure
Lauric acid	Dodecanoic acid	143-07-7	12:0	$C_{12}H_{24}O_2$	200.32	
Myristic acid	Tetradecanoic acid	544-63-8	14:0	$C_{14}H_{28}O_2$	228.38	
Myristoleic acid	*cis*-9-Tetradecenoic acid	544-64-9	14:1	$C_{14}H_{26}O_2$	226.26	
Palmitic acid	Hexadecanoic acid	57-10-3	16:0	$C_{16}H_{32}O_2$	256.43	
Palmitoleic acid	*cis*-9-Hexadecanoic acid	373-49-9	16:1	$C_{16}H_{30}O_2$	254.42	
Stearic acid	Octadecanoic acid	57-11-4	18:0	$C_{18}H_{36}O_2$	284.48	
Oleic acid	*cis*-9-Octadecenoic acid	112-80-1	18:1	$C_{18}H_{34}O_2$	282.47	
Linoleic acid	*cis*-9,12-Octadecadienoic acid	60-33-3	18:2	$C_{18}H_{32}O_2$	280.46	
Linolenic acid	*cis*-9,12,15-Octadecatrienoic acid	463-40-1	18:3	$C_{18}H_{30}O_2$	278.44	
Arachidic acid	Eicosanoic acid	506-30-9	20:0	$C_{20}H_{40}O_2$	312.54	
Gondoic acid	*cis*-11-Eicosenoic acid	5561-99-9	20:1	$C_{20}H_{38}O_2$	310.53	
Behenic acid	Docosanoic acid	112-85-6	22:0	$C_{22}H_{44}O_2$	340.60	
Erucic acid	*cis*-13-Docosenoic acid	112-86-7	22:1	$C_{22}H_{42}O_2$	338.58	

be unreliable, though it warrants further investigation, since even 2% of this heavy paraffinic species could lead to concerns about low temperature performance of biodiesel.

As indicated by relatively large standard deviations, the composition of yellow grease is more variable than that of most other feedstocks. The heterogeneous nature of yellow grease has also been noted by Knothe and Steidley [15]. This is expected, because yellow grease is not a well defined, single material, but is composed of used cooking oil from various sources. Hence, yellow grease could resemble corn oil, canola oil, sunflower oil, olive oil, or several other food-grade oils.

2.2. Compositional profiles of biodiesel from algal lipids

Numerous algal strains have been investigated as potential sources of triglyceride feedstocks for biodiesel production. Due to their rapid growth rates, high lipid contents, tolerance for poor quality water, use in cleaning-up wastewater effluents, and other favorable qualities, interest in developing algal feedstocks for biodiesel continues to increase [16–20]. A comprehensive investigation of algae as a biodiesel feedstock was conducted by the National Renewable Energy Laboratory (NREL), who maintained an active Aquatic Species Program (ASP) from 1978 to 1996. The ASP final closeout report was issued in 1998, and remains an excellent source of information about growth conditions, productivities, and compositional profiles of various algal strains [21]. Recently, NREL and DOE have resumed investigations of algal fuels and have issued a technical roadmap for establishment of a domestic, commercial-scale algae-based biofuels industry [22,23].

Despite tremendous interest in algal feedstocks for biodiesel, the literature contains relatively few reports of detailed compositional profiles of the triglyceride fractions in algal lipids. It is known that for some algal strains, the FA compositional profiles are highly influenced by specific growth conditions such as nutrient levels, temperatures, and light intensities [18]. This makes it more difficult to define a single compositional profile for algal-based biodiesel, as compared to vegetable oil-based biodiesel. Also, although many different algal materials have been investigated, the exact species is often unknown, or mixed species are used. In addition, there are relatively few instances of the same algal species being characterized by more than one research group.

Table 3
Fatty acid compositional profiles of biodiesel (FAME) from fats and oils.

Fatty Acid		Camelina		Canola		Coconut		Corn		Jatropha		Palm		Rapeseed		Safflower		Soy		Sunflower		Tallow		Yellow Grease	
Common Name	Abbrev.	mean	dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev	mean	Dev
Capriotic	6:0					0.6	0.3															0.1			
Caprylic	8:0					6.8	1.9					0.8	1.3												
Capric	10:0			0.1		5.4	1.1					0.5	0.9	0.6								0.1			
Lauric	12:0	0.4				47.7	5.4			0.1	0.2	0.3	0.3	0.1	0.1			0.1	0.2	0.1	0.3	0.2	0.1	0.2	0.6
Tridecylic	13:0																								
Myristic	14:0	2.7	3.6			18.5	1.3			0.3	0.5	1.1	0.5	0.0	0.0	0.1	0.1	0.1	0.2	0.1	0.1	2.6	0.7	0.8	0.6
Myristoleic	14:1																					0.3	0.2		
Pentadanoic	15:0																					0.6	0.3	0.1	
Pentadecenoic	15:1																					0.1			
Palmitic	16:0	6.1	1.5	4.2	1.0	9.1	1.7	11.5	1.7	14.9	2.1	42.5	3.2	4.2	1.1	8.2	1.7	11.6	2.0	6.4	1.8	24.3	2.8	16.5	5.6
Palmitoleic	16:1			0.3	0.3	0.1	0.2	0.2	0.2	1.0	0.5	0.2	0.1	0.1	0.1	0.1		0.2	0.3	0.1	0.1	2.6	1.0	0.9	1.1
Hexadecadienoic	16:2																								
Hexadecatrienoic	16:3																								
Heptadecanoic	17:0			0.1						0.1		0.1		0.1				0.1	0.1	0.1		1.4	0.2	0.1	0.1
Heptadecenoic	17:1			0.1				0.1												0.1		0.6	0.3	0.1	
Stearic	18:0	2.8	0.4	2.0	0.4	2.7	0.7	1.9	0.3	6.1	1.7	4.2	1.1	1.6	0.7	2.5	1.0	3.9	0.8	3.6	1.1	18.2	4.5	7.1	3.9
Oleic	18:1	16.8	3.0	60.4	2.9	6.8	2.1	26.6	2.2	40.4	6.7	41.3	2.9	59.5	7.8	14.2	3.2	23.7	2.4	21.7	5.3	42.2	4.1	44.6	9.3
Linoleic	18:2	17.0	2.3	21.2	1.8	2.1	1.4	58.7	2.8	36.2	6.1	9.5	1.8	21.5	2.8	74.3	8.3	53.8	3.5	66.3	7.6	4.4	2.9	25.1	10.3
Linolenic	18:3	35.6	3.4	9.6	2.1	0.1	0.1	0.6	0.4	0.3	0.2	0.3	0.1	8.4	1.3	0.1	0.1	5.9	2.6	1.5	2.6	0.9	0.7	1.1	1.1
Stearidonic	18:4																					0.4		0.5	
Arachidic	20:0	1.4	1.3	0.7	0.3	0.1	0.1	0.3	0.2	0.2	0.1	0.3	0.1	0.4	0.5	0.1	0.1	0.3	0.3	0.3	0.2	0.2	0.1	0.3	0.1
Gondoic	20:1	14.4	2.8	1.5	0.2	0.0		0.1		0.1		0.1	0.1	2.1	3.0			0.3	0.1	0.2	0.2	0.6	0.2	0.5	0.1
Eicosadiensic	20:2	1.5	0.2	0.1										0.1											
Eicosatrienoic	20:3	0.8																							
Eicosatetraenoic	20:4																								
Eicosapentaenoic	20:5																								
Behenic	22:0	0.9	0.6	0.3	0.1			0.1	0.1	0.2	0.1	0.1		0.3	0.3			0.3	0.2	0.6	0.4	0.1	0.1	0.4	0.2
Erucic	22:1	3.1	0.8	0.5	0.2	0.0	0.0	0.1	0.1	0.1	0.1	0.0		0.5	0.5			0.1	0.1	0.1	0.1	0.1		0.1	0.1
Docosatetraenoic	22:4					0.0																			
Docosapentaenoic	22:5																								
Docosahexaenoic	22:6																								
Lignoceric	24:0	0.7	0.5	0.2	0.1	0.0		0.1	0.1	2.6	3.5	0.1		0.1				0.1	0.1	0.2	0.2			0.2	0.2
Nervonic	24:1	0.2		0.2		1.0				0.1				0.1	0.1			0.3	0.6					4.4	
Other/Unknown		1.0		2.2				0.3		1.2	1.1	0.9	0.9	4.3	4.4	0.8	0.8	4.1	4.7	0.1		2.0	1.2		
Total		104.1		101.2		101.1		100.2		102.7		101.2		99.9		99.5		100.8		101.2		100.0		103.1	
No. of References		6		14		14		12		20		27		20		9		39		18		16		19	

Dominant species in FAME Composition; Other major species (>= 10%) in FAME composition

Table 4
Literature references used to determine FA compositions of biodiesel produced from vegetable oil and animal fat feedstocks.

Feedstock	References
Camelina	[138,139,140,141,142,143]
Canola	[138,144,79,88,145,146,98,147,148,149,142,150,151,152]
Coconut	[138,153,154,155,156,157,158,148,149,159,151,160,161,162]
Corn	[138,163,41,88,156,95,149,159,164,165,166,167]
Jatropha	[168,138,169,170,171,172,13,173,174,175,157,176,177,178,179,180,181,182,183,184,185]
Palm	[186,168,187,138,163,41,79,76,188,153,154,155,75,96,98,189,156,157,158,176,71,95,148,149,142,151,165,166]
Rapeseed	[186,97,168,190,163,41,76,191,192,153,139,96,156,158,193,71,95,148,149,159,166,167,194]
Safflower	[156,193,71,148,149,159,195,167,194]
Soybean	[196,186,197,198,199,138,200,163,41,79,76,201,202,88,192,188,153,75,96,98,203,156,204,205,77,158,193,95,148,206,159,142,151,164, 207,152,166,167,194]
Sunflower	[208,138,163,88,98,209,156,210,176,193,95,148,149,159,164,166,167,194]
Tallow	[168,138,79,209,211,193,55,212,148,149,213,159,207,152,166,214]
Yellow grease	[97,208,215,216,138,217,218,200,163,192,145,146,75,219,204,216,55,151,214]

Over 40,000 algal species have been identified, with many more remaining unidentified [18]. Algae are often classified into the following major groupings:

- Cyanobacteria (Cyanophyceae)
- Green algae (Chlorophyceae)
- Yellow-green algae (Xanthophyceae)
- Golden algae (Chrysophyceae)
- Red algae (Rhodophyceae)
- Brown algae (Phaeophyceae)
- Diatoms (Bacilleriophyceae)
- Pico-plankton (Eustigmatophyceae)

Most algae that have been investigated as potential biodiesel feedstocks are green algae (Chlorophyceae), although several other types have also been reported. Triacylglycerides are the desired component within algal lipids for use as biodiesel feedstocks. However, these lipids typically also contain lesser amounts of wax esters, sterols, tocopherols, hydrocarbons, and others compounds. Just as with the vegetable oil feedstocks described earlier, triglyceride production within algae varies considerably from one species to the next. For algae, this is typically represented as the total lipid content, expressed as mass percent on a dry basis. As shown in Fig. 2, reported lipid contents vary widely, from less than 10% to over 50%. One reason for the large range of values for each species is that lipid content also varies as a function of growth conditions. However, lipid content alone does not define the total productivity of an algal strain, as productivity is the product of lipid content and algal growth rates [24].

Table 5
identifies 12 algal species having FA compositional profiles reported in the literature, and provides average profile data for each one. The literature sources used to define these average profiles are given in Table 6. In several cases, only one or two literature references were found to give the FA profiles; in no case were more than five references found. Consequently, these profiles should be regarded as having high uncertainty – even more so when considering that algal compositions also vary significantly depending upon growth conditions. For these algal FA compositions, no effort was made to identify and eliminate outliers, or to manipulate the data in any other way.

Average compositional profiles of the 12 algal species investigated are shown graphically in Fig. S-2. Comparison with the vegetable oil FA profiles reveals several interesting features. First, although most of these algal species have considerable amounts of C_{16} and C_{18} species, they are not as dominated by these species as are most vegetable oils. Second, some (but not all) algal FA profiles are broader than those of vegetable oils, containing significant amounts of both lighter species (C_{12}–C_{14}) and heavier species (C_{20}–C_{22}). Third, many (but not all) of the algal profiles contain substantial amounts of highly unsaturated species, including FAs with 3–6 double bonds. A useful comparison between animal fats/vegetable oils and algal lipids with respect to saturated and unsaturated compounds is provided in Fig. 3. As discussed below, the substantial levels of highly unsaturated constituents in many algal species have important implications with respect to biodiesel properties.

3. Biodiesel properties

The physical and chemical properties of biodiesel are determined by the compositional profiles described above. Biodiesel properties can vary substantially from one feedstock to the next. Specific variations with feedstock are discussed below in greater detail. However, it is also useful to briefly compare a few critical properties of biodiesel fuels as a class, with the properties of petroleum diesel, as shown in Table 7. For completeness, typical properties of renewable diesel are also included. (A thorough comparison of biodiesel and renewable diesel with respect to production, properties, and impacts has recently been published [25].) The property values shown in Table 7 were derived by combining information from several literature sources [8,26–32]. The properties of individual fuels can vary from those shown here.

Because of its considerable oxygen content (typically 11%), biodiesel has lower carbon and hydrogen contents compared to diesel fuel, resulting in about a 10% lower mass energy content. However, due to biodiesel's higher fuel density, its volumetric energy content is only about 5–6% lower than petroleum diesel. Typically, biodiesel has somewhat higher molecular weight than petroleum diesel, which is reflected in slightly higher distillation temperatures (as measured by T_{90}). Consisting mainly of straight chain esters, most biodiesel fuels have excellent cetane numbers – typically higher than No. 2 diesel fuel. The viscosity of most biodiesel fuels is significantly higher than petroleum diesel, often by a factor of 2.

Renewable diesel consists mainly of paraffinic hydrocarbons, usually dominated by odd carbon numbers [8,26,33]. (Depending upon process variables, even carbon number hydrocarbons can also be produced.) While some renewable diesel fuels contain primarily straight-chain, normal paraffins, others contain appreciable amounts of branched paraffins. As a consequence of their high paraffinic content, renewable diesel fuels typically have cetane numbers much higher than biodiesel. On a mass basis, the energy content of renewable diesel is higher than biodiesel (similar to petroleum diesel); on a volumetric basis, the energy contents of biodiesel and renewable diesel are very similar.

When reviewing the properties of biodiesel prepared from different feedstocks, it is useful to bear in mind the standard specifications that have been established by various fuel standard-setting

Table 5
Fatty acid (FA) compositional profiles of algal lipids.

Fatty acid		Bacillariophyta						Chlorophyta											
Common name	Abbrev.	*C. calcitrans*		*S. costatum*		*P. tricornutum*		*C. reinhardtii*		*C. vulgaris*		*D. salina*		*D. teriolecta*		*S. obliquus*		*N. oleabundans*	
		Mean	Dev	Mean	Dev	Mean	Dev	Mean	Dev	Mean	Dev	Mean	Dev	Mean	Dev	Mean	Dev	Mean	Dev
Capriotic	6:0									0.2				0.1					
Caprylic	8:0									0.6									
Capric	10:0					24.6				0.5				0.4		1.0			
Lauric	12:0									2.7		1.5		1.9	2.0	0.5			
Tridecylic	13:0									0.7				1.8		0.2			
Myristic	14:0	18.6		14.6	2.6	7.5	3.7	2.3		2.5	1.1	0.6	0.1	1.0	0.6	0.9	0.9	1.9	1.7
Myristoleic	14:1			0.4	0.0	25.5	36.0			0.9		0.4	0.4	0.7	0.8	21.7		0.4	
Pentadanoic	15:0			2.7		8.0	9.8					1.9		9.4	11.9	2.3		1.4	
Pentadecenoic	15:1									2.4				2.4		6.2			
Palmitic	16:0	26.3		12.4	4.2	15.4	4.0	32.4		17.4	10.6	19.4	2.3	13.2	9.7	11.6	14.4	36.3	33.2
Palmitoleic	16:1	27.5		22.8	4.5	22.6	3.8	1.7		3.1	2.3	1.7	1.1	5.5	4.5	5.6	0.6	2.5	0.9
Hexadecadienoic	16:2			4.1	2.1	4.4	1.2	1.6		8.1	5.6	1.5		2.7	0.6	3.2	1.2	2.1	0.6
Hexadecatrienoic	16:3			10.2	0.2	8.3	5.4	2.1		2.6	1.6	7.2	4.4	2.8	1.7	0.7		1.0	
Heptadecanoic	17:0			0.3		0.1				3.9				1.4		20.4		11.7	
Heptadecenoic	17:1									31.6				4.1		1.2		1.0	
Stearic	18:0	2.6		1.8	0.6	1.8	1.2			1.0	0.4	1.5		2.6	3.3	10.0	13.5	5.0	5.3
Oleic	18:1	4.5		2.9	0.4	5.5	6.5	17.7		9.2	4.4	5.3	2.6	5.7	4.3	9.5	11.8	23.4	11.4
Linoleic	18:2	0.8		1.4	0.3	1.6	0.8	10.8		20.7	19.6	6.2	0.1	14.2	9.6	17.5	6.0	10.2	4.0
Linolenic	18:3			0.9	0.9	0.9	0.7	21.6		14.3	12.0	38.7	1.0	35.0	6.1	1.9	2.6	10.0	10.6
Stearidonic	18:4			2.4	0.8	0.5						0.7		1.3		0.2		2.1	
Arachidic	20:0					1.3				1.5	2.0					2.0		2.1	
Gondoic	20:1					0.5	0.1			0.9								2.5	
Eicosadiensic	20:2			0.2		0.5	0.5					0.1				0.4			
Eicosatrienoic	20:3					0.1				0.8									
Eicosatetraenoic	20:4			1.4		2.2	2.2			0.4	0.2			0.3	0.0				
Eicosapentaenoic	20:5	6.7		14.2	1.7	26.1	11.0			0.5		0.1		0.4					
Behenic	22:0																		
Erucic	22:1																		
Docosatetraenoic	22:4																		
Docosapentaenoic	22:5																		
Docosahexaenoic	22:6	0.6		2.1	0.4	0.9	0.3			0.5									
Lignoceric	24:0																		
Nervonic	24:1																		
Total		87.6		94.4		158.1		90.0		107.0		86.6		127.0		116.9		113.7	
No. of references		1		2		5		1		4		2		4		2		3	

Table 5 (*Continued.*)

Fatty Acid		Cryptophyta		Eustigmatophyta		Haptophyta	
Common name	Abbrev.	*C. salina*		*N. oculata*		*I. galbana*	
		Mean	Dev	Mean	Dev	Mean	Dev
Capriotic	6:0						
Caprylic	8:0						
Capric	10:0						
Lauric	12:0	3.6	3.9				
Tridecylic	13:0						
Myristic	14:0	20.4	14.8	3.7	0.2	10.6	5.3
Myristoleic	14:1	0.3		0.2		0.0	
Pentadanoic	15:0	3.5	4.2	1.8			
Pentadecenoic	15:1						
Palmitic	16:0	16.7	2.8	24.9	10.0	13.8	2.5
Palmitoleic	16:1	1.8	0.6	23.3	3.8	9.8	10.3
Hexadecadienoic	16:2	0.7		0.8			
Hexadecatrienoic	16:3			0.6			
Heptadecanoic	17:0	1.1	0.4	1.1			
Heptadecenoic	17:1						
Stearic	18:0	2.2	0.9	2.1	1.5	1.2	0.1
Oleic	18:1	12.8	6.8	5.8	1.8	15.7	8.3
Linoleic	18:2	9.3	10.0	3.6	3.3	4.4	2.4
Linolenic	18:3	8.5	2.8	3.8	4.1	2.9	2.0
Stearidonic	18:4	11.4	16.4			13.8	6.8
Arachidic	20:0						
Gondoic	20:1	0.2	0.1				
Eicosadiensic	20:2			0.1			
Eicosatrienoic	20:3			0.4	0.1		
Eicosatetraenoic	20:4	1.8	1.4	4.5	0.8	0.5	
Eicosapentaenoic	20:5	5.0	6.9	27.6	10.8	13.1	17.7
Behenic	22:0						
Erucic	22:1						
Docosatetraenoic	22:4	0.1					
Docosapentaenoic	22:5					1.2	
Docosahexaenoic	22:6	2.9	3.7			14.4	5.4
Lignoceric	24:0						
Nervonic	24:1					2.3	
Total		102.0		104.3		101.2	
No. of References		3		3		3	

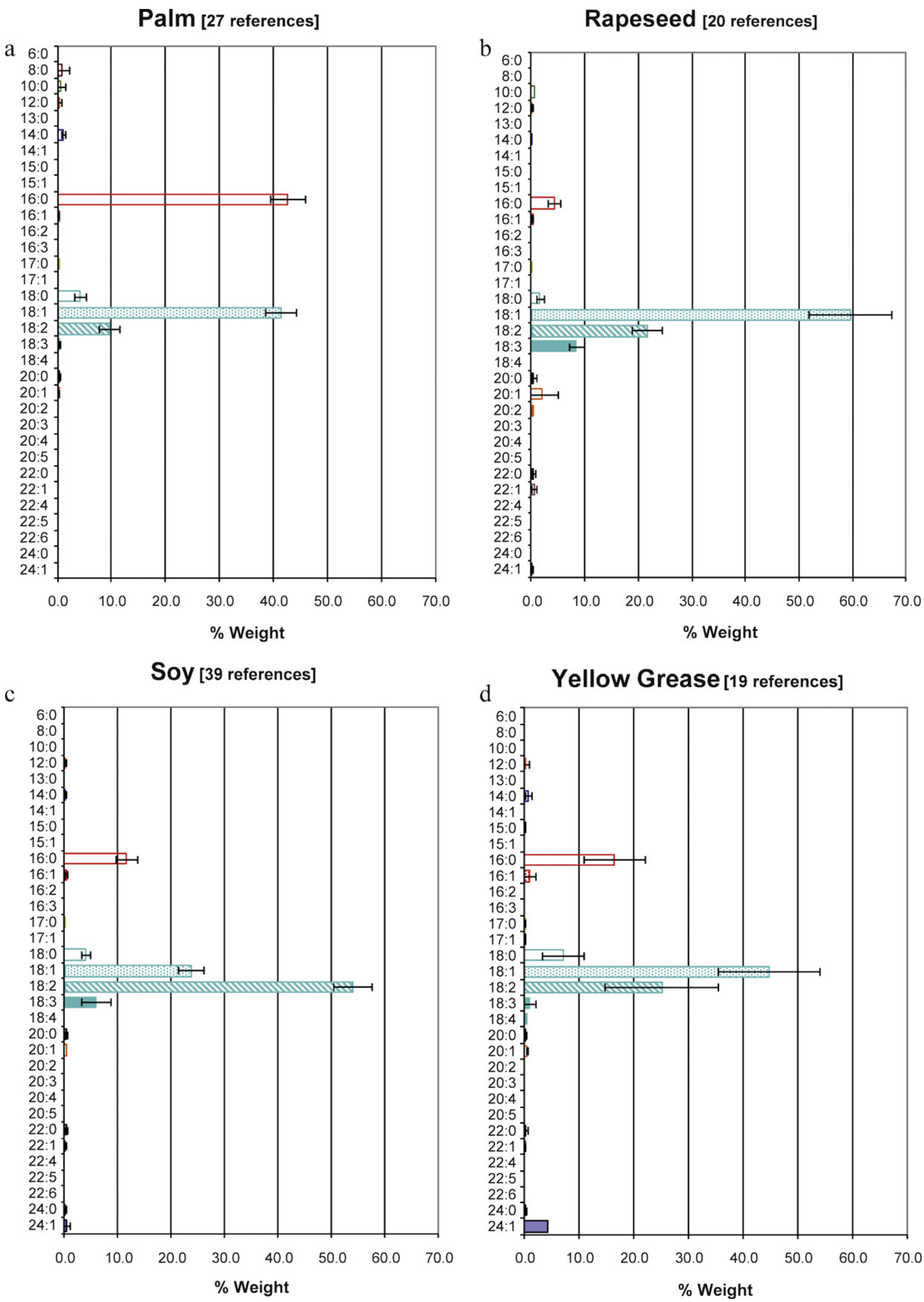


Fig. 1. Compositional profiles of fatty acids from (a) palm oil, (b) rapeseed oil, (c) soy oil, and (d) yellow grease.

organizations, particularly ASTM (in the U.S.) and the European Committee for Standardization (CEN). ASTM has established standard specifications for biodiesel fuel blendstocks (B100) for middle distillate fuels, called ASTM D6751 [7], as well as for biodiesel blends of B6 to B20 in petroleum diesel, called ASTM D7467 [34]. Blends of B5 and below are permitted under the standard specifications for No. 2 diesel fuel, ASTM D975 [35]. To date, the CEN has only established standard specifications for B100, called EN 14214

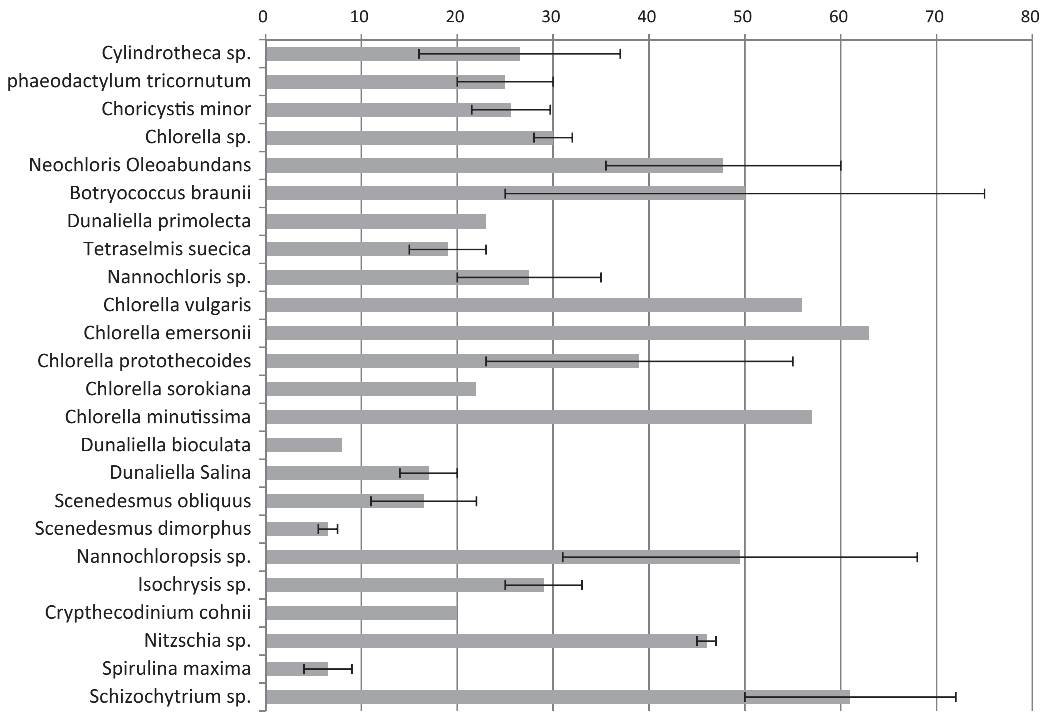


Fig. 2. Lipid contents reported for various algal species, wt.%.
Confidence intervals are min. and max. of reported values. Data taken from [18,134,226,19,336].

[36,37], but not for mid-level blends such as B20. The European standard specifications for conventional No. 2 diesel fuel (EN 590) permit blends of B7 and below; and deliberations are underway to allow an increase to B10 [32]. Table 8 provides a side-by-side listing of specifications for biodiesel blendstock (B100; ASTM and CEN) and mid-level biodiesel blends (B6–B20; ASTM only). For each specification, both the limits and the methods are shown.

Table 6
Literature references used to determine FA compositions of biodiesel produced from algal feedstocks.

Microalgae feedstocks		References
Bacillariophyta	Chaetoceros calcitrans	[220]
	Skeletonema costatum	[221,222]
	Phaeodactylum tricornutum	[223,224,220,40,222]
Chlorophyta	Chlamydomonas reinhardtii	[225]
	Chorella vulgaris	[226,227,40,225]
	Dunaliella salina	[228,222]
	Dunaliella teriolecta	[226,40,225,222]
	Scenedesmes obliquus	[226,40]
	Neochloris oleabundans	[229,230,226]
Cryptophyta	Chromonas salina	[231,232,222]
Eustigmatophyta	Nannochloropsis oculata	[233,229,222]
Haptophyta	Isochrysis galbana	[224,229,234]

Table 7
Typical properties of biodiesel compared to petroleum diesel and renewable diesel.

Property	No. 2 petroleum diesel	Biodiesel (FAME)	Renewable diesel
Carbon, wt.%	86.8	76.2	84.9
Hydrogen, wt.%	13.2	12.6	15.1
Oxygen, wt.%	0.0	11.2	0.0
Specific Gravity	0.85	0.88	0.78
Cetane no.	40–45	45–55	70–90
T_{90}, °C	300–330	330–360	290–300
Viscosity, mm^2/s. @ 40 °C	2–3	4–5	3–4
Energy content (LHV)			
Mass basis, MJ/kg	43	39	44
Mass basis, BTU/lb.	18,500	16,600	18,900
Vol. basis, 1000 BTU/gal	130	121	122

3.1. Properties of biodiesel from fats and oils

Table 9 summarizes several of the most important physical/chemical properties of biodiesel (FAME) derived from the same 12 feedstocks whose compositional profiles were discussed above. These data were obtained using a similar process as with the fatty acid (FA) profile data. Numerous literature sources (identified in Table 10) were reviewed to create these profiles. The number of references for a given FAME varied from 4 (for safflower) to 59 (for soy).

FAME property values reported by different authors vary considerably. As with the FA compositional profiles, this variation in properties is largely attributed to use of different analytical methods and different skill levels in applying these methods. Additional sources of variability include the chemical process used to produce the FAME, the clean-up process used to purify raw FAME, and the storage time (and conditions) prior to analysis.

The oxidative stability of FAME is a critical in-use property of biodiesel, but was not considered in this summary of fuel properties because it is influenced greatly by the FAME clean-up and storage practices employed. In addition, some of the biodiesel samples contained anti-oxidant additives, which modified the inherent stability of the FAME material. There are several other FAME properties for which specifications have been established, but that also depend largely upon manufacturing and handling practices, rather than being inherent properties of FAME itself. These include water and sediment, methanol content, ash, metals, acid number, glycerine content, and cold soak filterability. Thus, these properties are not included in the summary Table 9.

Important properties that are directly related to FAME itself, and are reported frequently in the literature, include viscosity, cetane number, cloud point, pour point, cold filter plugging point, specific gravity, flash point, iodine value, and heating value. All these

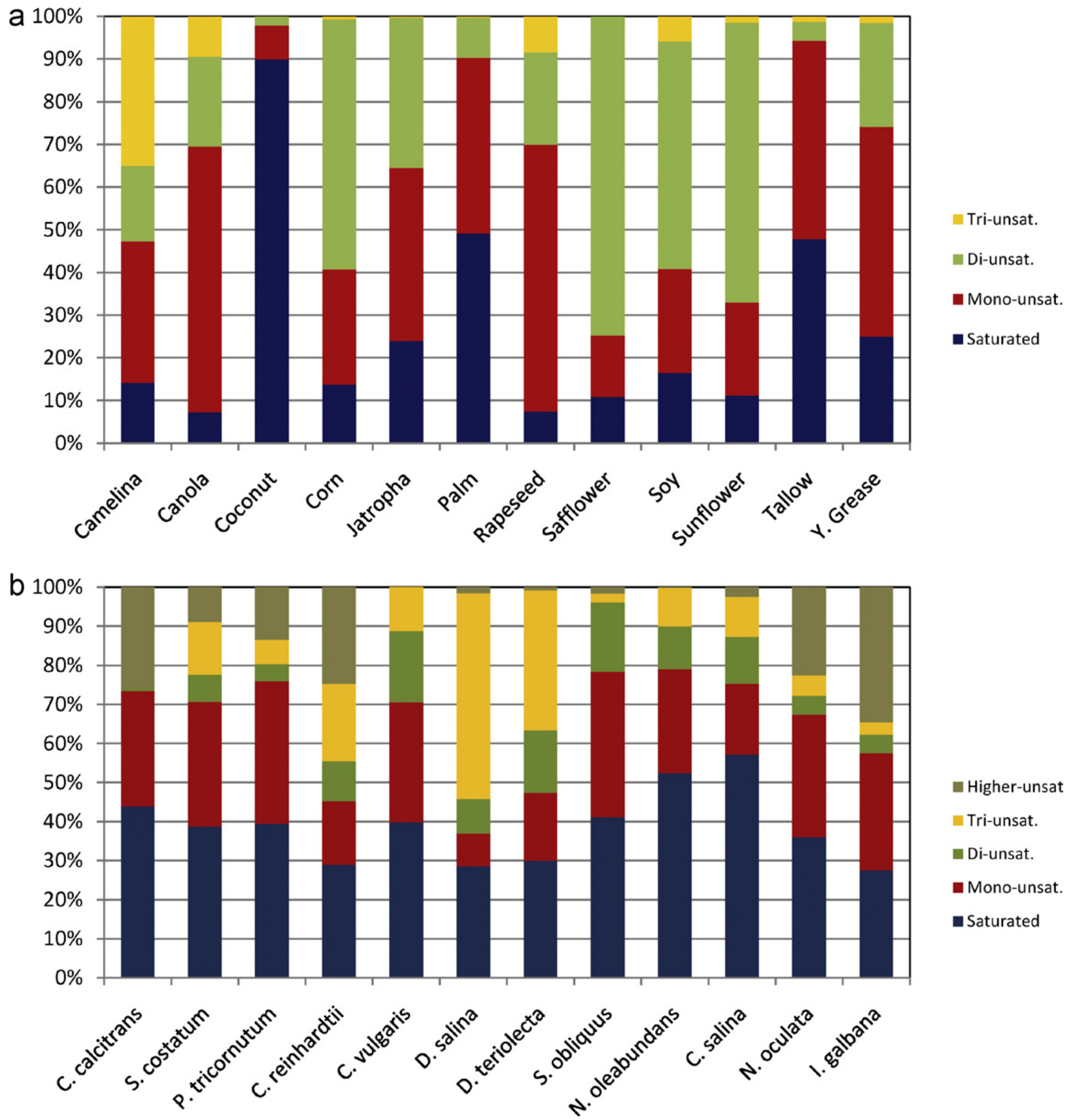


Fig. 3. Saturation/unsaturation profiles of biodiesel feedstocks from (a) animal fat and vegetable oil and (b) algal lipids.

properties are included in Table 9, along with cetane index (CI), which was reported by many authors. CI is commonly used to approximate the cetane number for petroleum mid-distillate fuels using formulas defined in test methods ASTM D976 and D4737. These formulas are based upon the fuel's density and distillation properties, both of which are quite different for biodiesel as compared to petroleum diesel. Because of this, the ASTM standard methods for CI should not be applied to biodiesel, and any reported biodiesel CI value derived from these methods should not be considered reliable. Nevertheless, CI values are included in this assessment to illustrate their lack of correlation with cetane numbers, and to highlight the unreliability of CI for biodiesel.

The approach taken in handling literature-reported biodiesel property data was similar to that described above for the FA profile data. Initially, all reported values were accepted, with no *a priori* judgment about data validity. From this raw data, a mean and standard deviation were computed for each FAME. More careful inspection of the data was then conducted, especially for values that were greatly different from the mean. In several cases, viscosity values were found to have been determined at temperatures other than the standard of 40 °C. Because viscosity varies greatly with temperature, values determined at non-standard temperature conditions were eliminated when determining means and standard deviations.

Sulfur values also required careful assessment. Many sources report values using older analytical methods meant for conventional diesel fuel, having sulfur levels of 500 ppm or higher. In such cases, results were often reported as <0.05% (or similar value). These relatively insensitive methods are not appropriate for ultra-low sulfur diesel (ULSD) or biodiesel. Therefore, sulfur values were only included in this review if they were determined by ASTM D5453 (or equivalent method), which is reliable in measuring ppm levels of sulfur.

Energy content is another important in-use property of FAME, though there is no specification for this in either U.S. or European biodiesel standards. Nevertheless, many authors reported values for energy content – although there is much inconsistency in the metrics used. For example, lower heating value (LHV), higher heating value (HHV), gross energy content, and net energy content were all reported – often without a clear definition of how the

Table 8
U.S. and European specifications for biodiesel (B100) and biodiesel blends.

Property	Biodiesel blendstock (B100)				B6–B20 Blends	
	U.S. (ASTM D6751-08)		Europe (EN 14214)		U.S. (ASTM D7467-08)	
	Limits	Method	Limits	Method	Limits	Method
Water and sediment (vol.%, max)	0.05	D 2709	0.05	EN 12937[g]	0.05	D 2709
Total contamination (mg/kg, max.)			24	EN 12662		
Kinematic viscosity @ 40 °C (mm²/s)	1.9–6.0	D 445	3.5–5.0	EN 3104/3105	1.9–4.1	D 445
Flash point, closed cup (°C, min)	93	D 93	101	EN 3679	52	D 93
Methanol (wt.%, max.)	0.20[a]	EN 14110	0.20	EN 14110		
Cetane no. (min)	47	D 613	51	EN 5165	40	D 613
Cloud point (°C)	Report[d]	D 2500	Country Specific[d]		Report[d]	D 2500
Sulfated ash (wt.%, max.)	0.020	D 874	0.020	EN 3987		
Total ash (wt.%, max.)					0.01	D 482
Gp I metals Na + K (mg/kg, max.)	5.0	EN 14538	5.0	EN 14108/14109		
Gp II Metals Ca + Mg (mg/kg, max.)	5.0	EN 14538	5.0	EN 14538		
Total Sulfur (ppm, max.)	15[b]	D 5453	10	EN 20846	15	D 5453
Phosphorous (ppm, max.)	10	D 4951	4	EN 14107		
Acid no. (mg KOH/g, max.)	0.50	D 664	0.50	EN 14104	0.3	D 664
Carbon residue (wt.%, max)	0.05	D 4530	0.30[e]	EN 10370	0.35[e]	D 524
Free glycerin (wt.%, max.)	0.02	D 6584	0.02	EN 14105/14106		
Total glycerin (wt.%, max.)	0.24	D 6584	0.25	EN 14105		
Mono glyceride (wt.%, max)			0.80	EN 14105		
Diglyceride (wt.%, max)			0.20	EN 14105		
Triglyceride (wt.%, max)			0.20	EN 14105		
Distillation (T_{90} °C, max.)	36[c]	D 1160			343	D 86
Copper strip corrosion (3-h at 50° C, max.)	No. 3	D 130	No. 1	EN 2160	No. 3	D 130
Oxidation Stability (h @ 110 °C, min)	3.0	EN 14112	6.0	EN 14112	6	EN 14112
Linolenic acid methyl ester (wt.%, max)			12.0	EN 14103		
Polyunsaturated acid methyl esters (wt.%, max)			1.0	prEN 15799		
Ester Content (wt.%, min)			96.5	EN 14103	6–20 vol.%	D 7371
Iodine Value (g I_2/100 g, max.)			120	EN 14111		
Density (kg/m³)			860–900	EN 3675		
Lubricity @ 60 °C, WSD, microns (max.)					520	D 6079
Cold Soak Filterability (seconds, max.)	360[f]	D 7501				

[a] Alternatively, flash point must be >130 °C.
[b] For blending with ULSD. For other fuels, higher sulfur levels are allowed.
[c] Atmospheric equivalent T-90 point.
[d] Low temperature properties are not strictly specified, but should be agreed upon by the fuel supplier or purchaser.
[e] This limit is based on the bottom 10% fraction of the fuel, not the entire fuel.
[f] 200 s max. for use in diesel blends at low temperature (<−12 °C).
[g] Method EN 12937 measures total water (in units of μg/g), but not sediment.

measurements were made. In some references, the specific metric being reported was not indicated. In such cases, the authors' judgment was used to assign the values as either LHV or HHV.

Two other "properties" of biodiesel shown in Table 9 were calculated based upon the average compositional profiles of the 12 FAME types: (1) average chain length and (2) average degree of unsaturation. Average chain length was computed by multiplying the mass fraction of each FA constituent times its associated carbon number, then summing over the entire profile. Similarly, average degree of unsaturation was computed by multiplying the mass fraction of each FA constituent times the associated number of carbon–carbon double bonds, then summing over the entire profile.

The average properties of the 12 biodiesel types considered are shown graphically in Fig. S-3, along with confidence intervals of ±1 standard deviation. These depictions provide insights into differences and similarities among the biodiesel fuels. For example, all 12 biodiesel types have very low sulfur contents, with no significant differences among them. All these biodiesels are well below the sulfur specification maximum in ASTM D6751 (15 ppm) and EN 14214 (10 ppm). Other properties are discussed below.

3.1.1. Kinematic viscosity

The kinematic viscosity data show that 10 of the 12 biodiesel types fall within a narrow range of 4–5 mm²/s. Biodiesel from camelina has slightly lower viscosity at 3.8 mm²/s, while coconut-derived biodiesel is substantially lower, at 2.75 mm²/s. The ASTM D6751 viscosity specification of 1.9–6.0 mm²/s is satisfied by all 12 biodiesels. The more restrictive EN 14214 specification of 3.5–5.0 mm²/s would exclude biodiesel from coconut oil.

3.1.2. Specific gravity

Specific gravity varied within a narrow range of 0.873–0.883 for all 12 biodiesel types. Palm-derived and coconut-derived FAME have the lowest specific gravity values of 0.873 and 0.874, respectively. The EN 14214 standard includes a density specification of 860–900 kg/m³. (*Note*: specific gravity and density are used interchangeably in this report.) Biodiesel produced from all 12 of these feedstocks would meet this specification. The ASTM D6751 standard does not include a specification for density.

3.1.3. Cold flow properties

All three low temperature properties considered [cloud point (CP), pour point (PP), and cold filter plugging point (CFPP)] show very similar patterns across the sets of 12 biodiesel types. In each case, biodiesel from palm oil and tallow show the poorest performance (highest temperature points), while biodiesel from rapeseed generally shows the best performance (lowest temperature points). Because of large seasonal and geographic temperature variability, neither the U.S. nor European biodiesel standards have firm specifications for these low temperature properties, though they are among the most important properties in determining the suitability of biodiesel fuels in-use.

Table 9
Physical/chemical properties of biodiesel (FAME) from fats and oils.

Property	Camelina		Canola		Coconut		Corn		Jatropha		Palm		Rapeseed		Safflower		Soy		Sunflower		Tallow		Yellow Grease	
	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev	mean	dev
Sulfur Content, ppm	2	2	2	0	3	1	4	1	5	6	2	2	4	3	ND		2	2	2	3	7	8	5	5
Kinematic Viscosity @ 40 °C, mm²/s	3.80	0.55	4.38	0.27	2.75	0.24	4.19	0.33	4.75	0.58	4.61	0.56	4.50	0.35	4.14	0.13	4.26	0.39	4.42	0.26	4.69	0.44	4.80	0.48
Cloud Point, °C	3	1	-2	1	-3	3	-3		5	3	14	2	-3	2	-4	2	0	2	2	1	13	2	8	5
Pour Point, °C	-7	3	-6	3	-9	5	-2	2	0	5	13	2	-10	3	-7	1	-4	3	-2	2	10	3	3	7
CFPP, °C	-3	2	-9	4	-5	1	-8	6	ND		9	5	-12	6	-6		-4	2	-2	1	13	2	1	5
Flash Point, °C	136		153	29	113	6	171	16	152	20	163	17	169	16	174	7	159	18	175	9	124	35	161	22
Cetane No.	50.4	1.6	53.7	1.5	59.3	9.7	55.7	2.9	55.7	3.0	61.9	3.6	53.7	2.9	51.1	1.8	51.3	4.6	51.1	3.2	58.9	2.1	56.9	4.2
Cetane Index*	ND		61.5		ND		60.9		ND		50.5	4.4	54.7	5.0	ND		52.3	5.7	55.0	8.4	59.1		48.5	
Iodine Value	152.8	2.5	108.8	1.3	18.5	16.3	101.0		109.5		54.0	6.1	116.1	6.7	141.0		125.5	5.4	128.7	4.6	65.9	15.6	88.9	16.2
Specific Gravity	0.882	0.007	0.883	0.003	0.874	0.001	0.883	0.005	0.876	0.009	0.873	0.008	0.879	0.010	0.879	0.012	0.882	0.007	0.878	0.011	0.878	0.006	0.879	0.010
Lower Heating Value, MJ/Kg	ND		38.9	1.6	35.2		39.9		37.7		37.3	2.3	37.6	1.6	ND		37.0	1.9	35.3	2.1	37.2	0.2	37.6	1.6
Higher Heating Value, MJ/Kg	45.2		41.3	3.1	38.1		43.1	2.7	40.7	1.5	40.6	1.5	41.1	2.3	42.2	2.7	39.7	0.8	40.6	2.4	39.7	0.2	39.4	1.1
Avg. Chain Length	19.10		18.20		13.40		17.80		18.30		17.20		17.90		17.80		17.90		18.10		17.30		18.50	
Avg. Unsaturation	1.81		1.34		0.12		1.46		1.15		0.62		1.31		1.63		1.50		1.59		0.59		1.06	
No. of References	7		15		7		6		23		44		39		4		59		20		12		37	

ND = No Data found in literature
* = No accepted method for determining cetane index of biodiesel

Table 10
Literature sources used to determine physical/chemical properties of biodiesel from vegetable oils and animal fats.

Feedstock	References
Camelina	[138,139,235,236,141,142]
Canola	[237,238,138,31,239,144,78,201,146,240,241,148,142,150,242]
Coconut	[138,243,155,148,160,161,162]
Corn	[138,163,240,86,242,95]
Jatropha	[244,245,168,246,73,138,247,248,89,169,249,250,251,252,253,240,171,172,13,173,254,176,177]
Palm	[186,255,256,257,258,245,48,259,168,260,73,261,138,163,262,263,264,79,76,265,169,266,267,268,155,269,75,96,270,271,189,272,273,274,176,86,71,95,275,148,276,142,61,277]
Rapeseed	[186,255,97,278,279,258,48,280,259,168,281,163,76,282,191,283,284,192,285,169,267,286,26,96,270,287,288,289,290,86,291,71,292,95,293,294,276,295,277]
Safflower	[289,86,71,296]
Soybean	[196,186,297,298,257,299,258,237,198,300,199,73,51,301,238,138,31,79,200,302,262,163,76,201,303,304,305,306,202,192,265,285,169,267,50,75,96,270,307,203,205,272,308,309,310,77,311,86,312,242,95,313,148,142,314,207,315,277,316]
Sunflower	[257,245,317,73,208,138,318,163,265,285,272,210,176,86,242,95,319,320,321,322]
Tallow	[257,237,168,138,79,201,265,272,212,207,323,211]
Yellow grease	[97,324,299,258,245,325,326,237,317,327,328,208,215,216,138,31,239,217,218,201,200,163,192,146,268,329,75,219,330,273,331,216,332,333,334,335,316]

3.1.4. Flash point

The flash point values for 11 of the 12 biodiesel types are well above the minimum specifications in the U.S. (93 °C) and European (101 °C) standards. Coconut-derived biodiesel has a significantly lower flash point, although it is still just within the standard specifications. The main purpose of the flash point specification is to ensure that the manufactured FAME has been sufficiently purified by removal of excess methanol. Even small amounts of residual methanol in FAME will cause a significantly depressed flash point.

3.1.5. Cetane number

Cetane number values for all 12 biodiesel types easily surpass the ASTM minimum specification of 47, with the highest cetane values being observed for palm-, coconut-, and tallow-derived FAME. The European specification is more stringent, requiring a minimum cetane number of 51. On this basis, biodiesel produced from camelina, safflower, soy, and sunflower are all borderline, and specific batches may have difficulty in meeting the specification.

3.1.6. Iodine value

Iodine value (IV) is a measure of unsaturation. ASTM D6751 does not include a specification for IV, while EN 14214 has a maximum IV specification of 120 mg I_2/100 g FAME. Rapeseed biodiesel is just below this value of 120, while biodiesel from soy and sunflower are just over the limit. Biodiesel from camelina and safflower have even higher IV levels, and would clearly be "off-spec" with respect to EN 14214, while all other biodiesel types investigated here are well below the 120 IV level. Coconut-derived biodiesel is highly saturated, and has an exceptionally low IV of about 19.

3.1.7. Heating value

Neither the U.S. nor European biodiesel standards include a specification for heating value. Due to its substantial oxygen content, it is generally accepted that biodiesel from all sources has about 10% lower mass energy content (MJ/kg) than petroleum diesel. However, there are some differences in heating value among the 12 biodiesel types investigated here. Camelina was reported to have the highest HHV at 45.2 MJ/kg (based upon a single report), followed by corn and safflower at 43.1 and 42.2 MJ/kg, respectively. FAME produced from soy, sunflower, tallow, and yellow grease are all just below 40 MJ/kg, while FAME from coconut is much lower at 38.1 MJ/kg. It should be emphasized that with several biodiesel types, the data reported for heating values is very sparse. In addition, confusion between LHV and HHV is likely in several literature reports.

3.1.8. Other properties

The calculated properties of average chain length and average degree of unsaturation were also investigated. Eleven of the 12 biodiesel fuels have average chain lengths varying from 17 to 19, with camelina-derived fuel being the longest at 19.1. Coconut-derived biodiesel has a considerably shorter average chain length of 13.4. The average degree of unsaturation varied substantially across the range of 12 biodiesel types – from a low of 0.12 (for coconut) to a high of 1.81 (for camelina). As discussed below, this variability in unsaturation is one of the most important factors in explaining many other differences in properties and performance among the range of biodiesel types.

3.2. Properties of biodiesel from algal lipids

Despite the current emphasis on use of algal lipids as biodiesel feedstocks, there are very few literature reports of actual biodiesel samples produced from algae, and even fewer reports of relevant fuel properties from such algal-derived materials. Miao et al. reported the production of biodiesel from *Chlorella protothecoides*, and showed that it satisfied several of the ASTM specifications for biodiesel [38,39]. Also, Francisco et al. produced biodiesel samples from six different algal species, and showed that they meet several of the specifications for European biodiesel – including iodine value (IV) [40]. Considering the high degree of unsaturation of many algal FA profiles (see Table 5 and Fig. 3) it is surprising that these biodiesels would meet the European IV specification. It is also expected that such highly unsaturated materials would have difficulty in meeting the oxidation stability requirements within either the U.S. or European biodiesel standards. Assessing the suitability of algal-derived FAME as a biodiesel fuel is clearly an area requiring further study.

3.3. Relationships between composition and properties

The physical and chemical properties of biodiesel are largely dictated by the specific compositional profile of the FAME material. Several researchers have investigated relationships between particular properties and compositional features by careful study of pure compounds, or mixtures of pure compounds [41,42]. In this study, considerable information has been compiled on properties and compositions of complete FAME products from many feedstocks, enabling investigation of relationships across a range of realistic biodiesel types.

As a first step, a simple correlation matrix utilizing the average physical/chemical properties of the different biodiesel types was developed. (Coconut-derived FAME was excluded from this analysis because it differed from the other 11 FAME materials in

many ways.) The derived correlation matrix is shown in Table 11. Highlighting (by different shading colors) is used to indicate correlation values exceeding 0.70, 0.80, and 0.90. This clearly demonstrates the important relationships between certain properties, and highlights the significance of the computed property, "average unsaturation," which is highly correlated with several other properties.

The two compositional features of FAME generally regarded as most important in determining fuel properties are FA chain length and degree of unsaturation. To explore these relationships more thoroughly using this robust set of FAME data, a set of graphical displays was generated in which the average of 11 fuel properties for the 12 biodiesel types are plotted against average chain length, and against average degree of unsaturation. Example graphs for 6 of the most important properties are shown in Fig. 4. Least-squares regression fits are included on each of the "degree of unsaturation" graphs, but not on the "average chain length" graphs, as these generally showed very low correlations. The results and implications from each case are discussed below.

3.3.1. Kinematic viscosity

Viscosity is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another [43]. This is a critical property because it affects the behavior of fuel injection. In general, higher viscosity leads to poorer fuel atomization [44]. High viscosity can cause larger droplet sizes, poorer vaporization, narrower injection spray angle, and greater in-cylinder penetration of the fuel spray [45–49]. This can lead to overall poorer combustion, higher emissions, and increased oil dilution. The viscosity of biodiesel is typically higher than that of petroleum diesel – often by a factor of two. The viscosity of biodiesel blends increases as the blend level (B-level) increases. (The viscosity of straight vegetable oil is much higher yet, and is the main reason why such oils are unacceptable as diesel blendstocks.)

It has been shown that in a light-duty, common rail injection system, higher viscosity FAME resulted in increased delay in start of injection, reduced injection volume, and increased injection variability [50]. Viscosity is greatly affected by temperature [51]. Hence, many of the problems resulting from high viscosity are most noticeable under low ambient temperature and cold-start engine conditions. A recent study has shown that as temperature is reduced, the distribution of B100 fuel among individual injectors within an injector assembly becomes very unequal [52]. This, in turn, could lead to engine performance and emissions problems.

Viscosity of individual FAME molecules is known to increase with FA carbon number [43,51,53]. However, as shown in Fig. 4a, the average carbon number of most common biodiesel types does not vary over a wide range. The effects of increased carbon number within the alcohol used to produce FAME are smaller and less certain. Several researchers have reported slight increases in viscosity upon changing the alcohol from methanol, to ethanol, to propanol [43,51,54–56].

A high degree of correlation between biodiesel density and viscosity has been noted in the literature, with higher density leading to lower viscosity [57]. However, the correlation between density and specific gravity from our data set (shown in Table 11) is not very high, with a value of −0.62. Viscosity correlates more strongly with the degree of unsaturation, with higher unsaturation leading to lower viscosity (although coconut-derived FAME is an exception). Furthermore, the double bond configuration influences viscosity, with *trans* configuration giving higher viscosity than *cis* [43,53]. Most natural oils are dominated by *cis* double bonds, but some yellow grease (waste cooking oils) can have substantial levels of the *trans* configuration [53]. The location of the double bond within the FA chain apparently has little influence on viscosity.

Table 11
Correlations among biodiesel fuel properties.

Properties	Sulfur	Vis.	CP	PP	CFPP	Flash Point	Cetane No.	Cetane Index	Iodine Value	Specific Gravity	LHV	HHV	Avg. Chain Length	Avg. Unsat.
Sulfur	1.00													
Viscosity	0.60	1.00												
Cloud Point	0.43	0.57	1.00											
Pour Point	0.42	0.59	0.93	1.00										
CFPP	0.46	0.48	0.96	0.93	1.00									
Flash Point	-0.45	-0.04	-0.51	-0.32	-0.52	1.00								
Cetane No.	0.49	0.69	0.77	0.87	0.69	-0.22	1.00							
Cetane Index	0.14	-0.51	-0.40	-0.29	-0.27	-0.28	-0.18	1.00						
Iodine Value	-0.50	-0.72	-0.75	-0.87	-0.70	0.21	-0.97	0.15	1.00					
Specific Gravity	-0.26	-0.62	-0.69	-0.68	-0.67	-0.08	-0.61	0.58	0.54	1.00				
Lower Heating Value	0.12	-0.29	-0.34	-0.19	-0.35	-0.05	0.20	0.52	-0.15	0.51	1.00			
Higher Heating Value	-0.41	-0.84	-0.41	-0.47	-0.38	-0.06	-0.42	0.63	0.56	0.44	0.66	1.00		
Avg. Chain Length	-0.32	-0.39	-0.34	-0.56	-0.44	-0.13	-0.59	-0.12	0.67	0.48	0.05	0.49	1.00	
Avg. Unsaturation	-0.59	-0.79	-0.82	-0.87	-0.76	0.35	-0.94	0.20	0.96	0.65	0.03	0.62	0.65	1.00

= Correlation factor ≥ .70
= Correlation factor ≥ .80
= Correlation factor ≥ .90

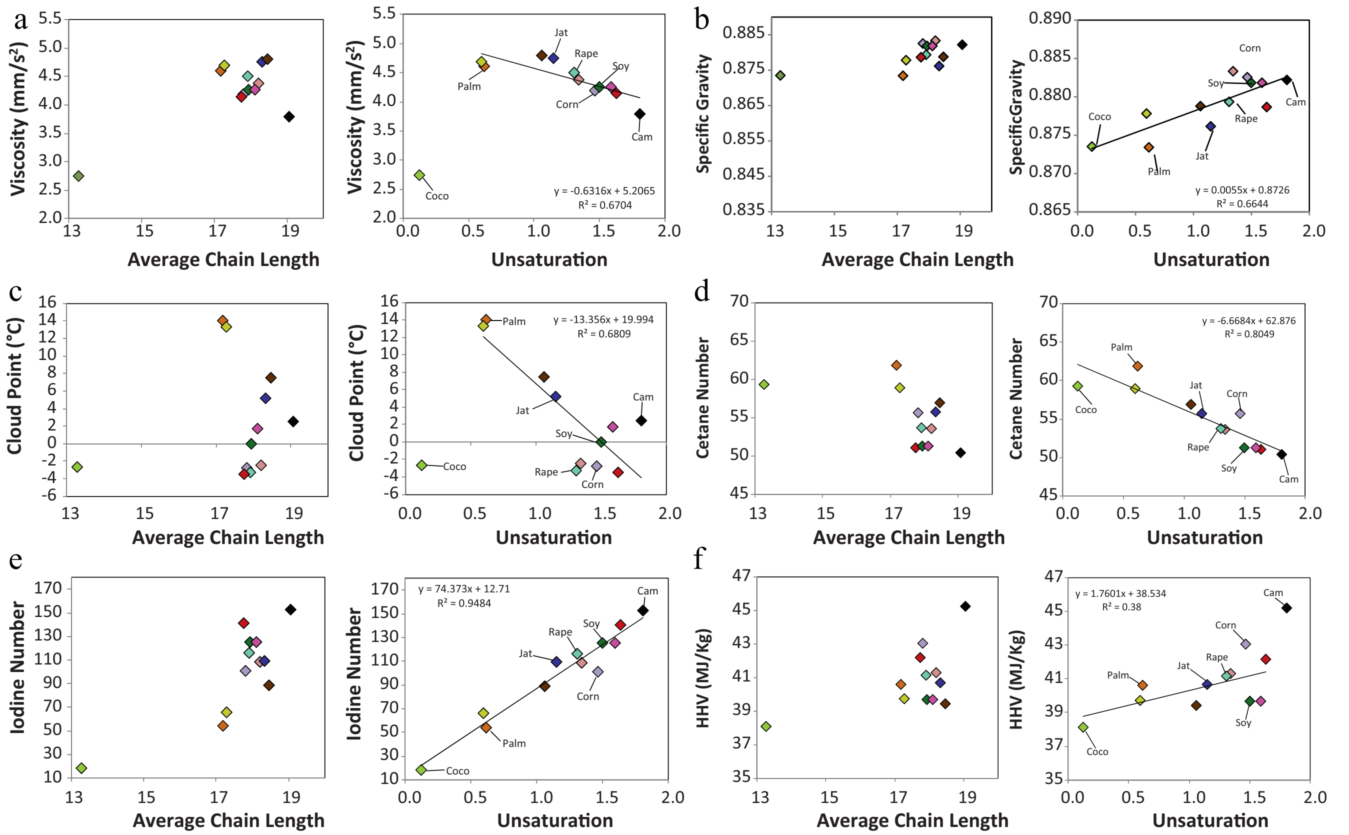


Fig. 4. Relationships between biodiesel unsaturation/chain length and other fuel properties: (a) kinematic viscosity, (b) specific gravity, (c) cloud point, (d) cetane number, (e) iodine value, and (f) higher heating value (HHV).

- Average unsaturation and chain length computed from compositional profiles in Table 3.
- Biodiesel feedstock abbreviations: Coco, coconut; Jat, Jatropha; Cam, camelina.

3.3.2. Density

Fuel density is a key property that affects engine performance. Because fuel injection pumps meter fuel by volume, not by mass, a greater or lesser mass of fuel is injected depending upon its density. Thus, the air–fuel ratio and energy content within the combustion chamber are influenced by fuel density.

In general, densities of biodiesel fuels are slightly higher than those of petroleum diesel, and increasing the B-level of biodiesel blends increases the blend's density. As shown in Fig. 4b, FAME density is strongly affected by the degree of unsaturation, with higher unsaturation leading to increased density [53]. (*Note*: in this study, density and specific gravity are used interchangeably. Specific gravity is most frequently reported in the literature, although density is the specification metric.) Table 11 shows the correlation coefficient between specific gravity and average unsaturation to be 0.65.

It has been reported that biodiesel density is also affected by chain length, with higher chain length leading to lower fuel density [53]. However, this does not appear to be the case for the set of 12 biodiesel fuels investigated here, as indicated by the data plotted in Fig. 4b, or by the correlation coefficients shown in Table 11. No literature information was found regarding the effect of alcohol length or branching upon density.

3.3.3. Cold flow properties

Low temperature performance is one of the most important considerations for users of biodiesel. Just as with conventional diesel fuel, precautions must be taken to ensure satisfactory low temperature operability of biodiesel and its blends [31]. Poor low temperature performance may be exhibited in several ways, but principally by filter plugging due to wax formation, and engine starving due to reduced fuel flow. There is no single best way to assess low temperature performance, and the existing fuel standards (both U.S. and European) do not include explicit specifications for cold flow properties – for either conventional diesel or biodiesel. However, the fuel provider is generally required to give an indication of the cold flow properties by reporting the cloud point (CP) of the fuel. A number of other laboratory tests are commonly used to define low temperature properties of biodiesel (and conventional diesel). These are listed in Table 12.

A good review of low temperature properties and performance of biodiesel is available in the literature [58]. In addition, a recent NREL publication provides useful guidance for addressing low temperature operability issues, as well as other in-use handling issues [31]. Poor cold flow properties result from the presence of long-chain, saturated FA esters present in biodiesel. Saturated methyl esters longer than C_{12} significantly increase CP and pour point (PP), even when blended with conventional diesel [59,60]. In general, the longer the carbon chain, the higher the melting point, and poorer the low temperature performance [53,56,61,62].

Table 12
Low temperature performance tests for biodiesel.

Test Name	Abbreviation	Test method(s)
Cloud point	CP	EN 23015, ASTM D2500, ASTM D5773
Pour point	PP	ASTM D97, ASTM D5949
Cold filter plugging point	CFPP	EN 116, IP 309, ASTM D6371
Low temp filterability test	LTFT	ASTM D4539
Wax appearance point	WAP	ASTM D3117
Cold soak filterability	–	ASTM D7501

Feedstocks with highly saturated FA structures (such as palm oil and tallow) produce biodiesel fuels with poor cold flow properties; whereas feedstocks with highly unsaturated fatty acid structures (such as rapeseed and safflower oil) produce fuels having better performance. Although the relationship between carbon chain length and low temperature properties is quite strong for pure FAME compounds, the effects appear more subtle when considering complex mixtures of FAME in actual biodiesel samples. For example, the CP results plotted in Fig. 4c do not reveal any significant correlation with average chain length. Very similar results are observed when using PP and cold filter plugging point (CFPP) as indicators of low-temperature performance. In fact, the three metrics of CP, PP, and CFPP are highly correlated amongst themselves, suggesting that any one could be used as an indicator of the others.

This analysis of complex FAME materials does not indicate a stronger relationship between chain length and low temperature properties because the metric of average chain length does not distinguish between saturated and unsaturated FA chains. Also, degree of unsaturation has a strong effect on low temperature properties, with higher unsaturation leading to greatly improved low temperature performance. Thus, the effect of unsaturation masks the effect of chain length in these FAME materials. More sophisticated data analysis techniques would be required to properly determine the separate effects of multiple variables upon fuel property relationships.

The relationship between CP and unsaturation is shown in Fig. 4c. Nearly identical results are observed when using PP or CFPP as indicators. Of these three low-temperature properties, only CP can be defined thermodynamically, as it is governed by solid–liquid equilibrium as a function of temperature. (True equilibrium conditions may not actually be achieved during the relatively rapid cool-down tests used to measure CP.) CP is the temperature at which the least soluble biodiesel component crystallizes from solution. Thus, in pure biodiesel, CP is determined by the type and amount of saturated fatty acid esters, with other components of biodiesel having little effect. Several researchers have developed predictive models for CP, based upon these thermodynamic relationships [63–65]. In general, these models show good agreement with laboratory measurements.

Wax crystallization is initiated by "close packing" of molecules. Thus, factors that disrupt or inhibit close packing of highly ordered molecules will decrease CP. Such structural disorder is increased with branching in either the FA chain or the alcohol portion of FAME [55,66]. Replacing methanol with ethanol to produce FAEE results in slightly improved low temperature performance, as ethyl esters typically have melting points 5–10 °C lower than the comparable methyl esters [65,67–70]. Introduction of a double bond also disrupts the close packing of molecules [53,62]. Furthermore, differences in double bond orientation have been noted, with the *cis* configuration providing better low temperature test performance than *trans* [71].

Increasing B-level of biodiesel typically leads to worsening of low temperature performance. However, blending of different components often results in non-linear effects with respect to low temperature properties [72]. For example, it has been reported that the very poor low temperature performance of palm-based biodiesel can be improved by blending with jatropha-based fuel [73,74].

In recent years, another low temperature operability problem has been recognized, resulting from the formation of insoluble particles upon storage at cool temperatures – though generally above the CP. These insolubles arise from precipitation of trace-level non-FAME impurities, not from the major FAME components themselves. Because of these operability problems, ASTM has adopted a new Cold Soak Filterability test within the biodiesel standard, D6751. The two major families of impurities identified as causing such precipitation problems are saturated monoglycerides and sterol glucosides [32,75–79]. Fig. 5 shows representative structures of these compounds.

3.3.4. Cetane number

Cetane number (CN) is a measure of a fuel's autoignition quality characteristics. Since biodiesel is largely composed of long-chain hydrocarbon groups (with virtually no branching or aromatic structures) it typically has a higher CN than petroleum diesel, and increasing the B-level of biodiesel blends increases the CN of the blend [80,81]. There are exceptions, however, when a relatively low CN biodiesel is blended with a relatively high CN petroleum diesel. In such cases, increasing B-level results in decreasing CN of the blend.

Biodiesel produced from feedstocks rich in saturated fatty acids (such as tallow and palm) have higher CN than fuels produced from less saturated feedstocks (such as soy and rapeseed). The effect upon CN of branching in the alcohol used to produce the biodiesel is very small, and difficult to discern [66,82]. The CN of pure FAME molecules increases with chain length, but this effect is masked when considering complex mixtures of FAME fuels. On the other hand, the CN of FAME fuels clearly varies with average degree of unsaturation (see Fig. 4d). The literature also reports that increasing degree of unsaturation leads to decreasing CN [53,66,81]. Lapuerta et al. have recently proposed a predictive equation for FAME CN that is largely driven by the number of double bonds in the FAME (as well as the FAME's carbon number) [83]. These authors also noted the high correlation between CN and iodine value (IV). This relationship is evident from the high correlation coefficient (−0.97) for CN and IV shown in Table 11.

It is noteworthy that no correlation between CN and cetane index (CI) is apparent. In addition, CI has no meaningful correlation with average unsaturation or IV. These observations suggest that CI values reported in the literature are not reliable, and highlight the problem that at present, a valid method for computing CI for biodiesel does not exist.

3.3.5. Iodine value

Iodine value (IV) is determined by measuring the amount of I_2 that reacts by addition to carbon–carbon double bonds; thus, IV is directly related to FAME unsaturation. This is clearly seen in Fig. 4e, and by the high correlation coefficient (0.96) in Table 11. IV was originally included as a specification in the European biodiesel standard, EN 14214, to ensure satisfactory oxidative stability of the fuel. However, IV is simply a measure of total unsaturation, while oxidative stability is more strongly influenced by the amount of FAME molecules having multiple double bonds (see Section 3.3.9). For this reason, there is some controversy about the need for an IV standard at all, and certainly about the rather restrictive maximum IV value of 120 g I_2/100 g biodiesel set by EN 14214.

The Worldwide Fuel Charter – established by a collection of U.S., European, and Japanese automobile manufacturer associations – also recommends an IV specification, but with a less restrictive allowable maximum of 130 g I_2/100 g biodiesel [84]. Some soy-derived biodiesel is likely to fail the European IV specification, but would more easily satisfy the higher IV recommendation by the Worldwide Fuel Charter. The ASTM biodiesel standard does not include an IV specification, believing that oxidative stability is better addressed by the Rancimat oxidative stability test (method EN 14112). Others have argued that there is no need for an IV specification because the cetane number specification effectively limits unsaturation [83].

3.3.6. Flash point

Flash point is inversely related to fuel volatility. The biofuel specifications for flash point are meant to guard against contamination

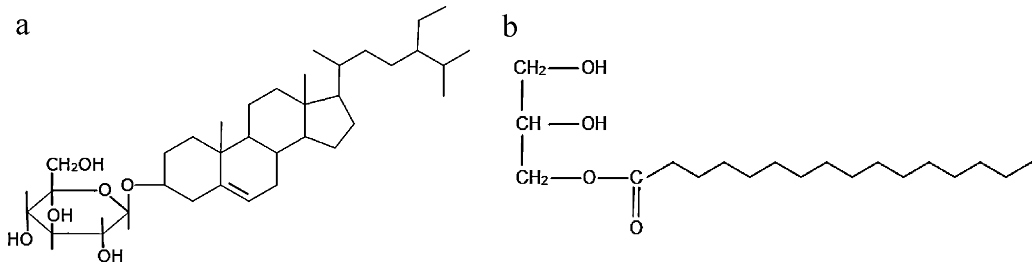


Fig. 5. Typical structures of compounds responsible for poor cold soak filtration: (a) sterol glucosides; (b) saturated mono-glycerides.

by highly volatile impurities – principally excess methanol remaining after product stripping processes. Of the 12 biodiesel materials investigated in this study, coconut-derived FAME showed the lowest inherent flash point, as expected, since its composition includes more light constituents ($\leq C_{12}$) than the other 11 FAMEs. Overall, our dataset does not indicate a high degree of correlation between flash point and any other property.

3.3.7. Heating value

Due to its high oxygen content, biodiesel has lower mass energy values than petroleum diesel. Therefore, increasing the B-level of biodiesel blends results in decreasing energy content. (The same relationships exist whether HHV or LHV is being considered.) As the FA carbon chain increases (for a constant unsaturation level) the mass fraction of oxygen decreases, so the heating value increases [85,86]. However, this increase in heating value with chain length is not readily apparent in the graph of Fig. 4f or the correlation matrix of Table 11.

Unsaturation level has a somewhat stronger influence upon heating values. Compared to saturated esters, unsaturated esters have lower mass energy content (MJ/kg), but higher volumetric energy content (MJ/gal.) [53]. This can be confusing, since mass energy content is typically measured in the laboratory, while fuel is metered and sold on a volumetric basis. The heating values plotted in Fig. 4f are on a mass basis (MJ/kg), and therefore might be expected to show a decrease with increasing unsaturation. In fact, no significant relationship is observed. Another point to remember is the confusing and inconsistent reporting of heating values in the literature. Further evidence of these problems is the rather low degree of correlation between LHV and HHV seen in the correlation matrix of Table 11.

3.3.8. Lubricity

Lubricity refers to the reduction of friction between solid surfaces in relative motion [30]. Two general mechanisms contribute to overall lubricity: (1) hydrodynamic lubrication and (2) boundary lubrication. In hydrodynamic lubrication, a liquid layer (such as diesel fuel within a fuel injector) prevents contact between opposing surfaces. Boundary lubricants are compounds that adhere to the metallic surfaces, forming a thin, protective anti-wear layer. Boundary lubrication becomes important when the hydrodynamic lubricant has been squeezed out or otherwise removed from between the opposing surfaces.

Good lubricity in diesel fuel is critical to protect fuel injection systems. In many cases, the fuel itself is the only lubricant within a fuel injector. With increasing operational demands of modern injection systems – due to higher pressures, injection rate shaping, multiple injections per cycle, and other features – maintaining adequate lubricity is more critical than ever. However, as the need for improved lubricity has increased, the natural lubricity of petroleum diesel fuels has decreased. The high degree of hydrotreatment necessary to produce ULSD effectively removes all hetero-atom containing molecules (O, N, and S) which have improved lubricity compared to hydrocarbons. In general, lubricity effectiveness decreases in the order of O > N > S > C [87].

Biodiesel from all feedstocks is generally regarded as having excellent lubricity, and the lubricity of ULSD can be improved by blending with biodiesel. Because of its naturally high lubricity, there is no lubricity specification for B-100 within either the U.S. or European biodiesel standards. However, the U.S. standard for B6–B20 blends (ASTM D7467) does include a lubricity specification, as does the conventional diesel fuel standard, ASTM D975. Low B-levels (often just 1–2%) typically provide satisfactory lubricity to ULSD [31,87].

In part, biodiesel's good lubricity can be attributed to the ester group within the FAME molecules, but a higher degree of lubricity is due to trace impurities in the biodiesel. In particular, free fatty acids and monoglycerides are highly effective lubricants [87,88]. It has been noted that purification of biodiesel by means of distillation reduces its lubricity because these impurities are removed. The effect of unsaturation upon lubricity is unclear, with some researchers reporting positive effects of carbon–carbon double bonds [87] while others report no effect [89].

The positive impact of biodiesel impurities upon lubricity is particularly noteworthy, as some of the same impurities (such as monoglycerides) are responsible for poor low temperature operability problems. Efforts to reduce these impurities (to improve low temperature properties) could have the unintended consequence of worsening lubricity.

3.3.9. Oxidative stability

Oxidative stability is one of the most important fuel properties with respect to in-use performance of biodiesel. Unstable fuel can lead to increased viscosity, as well as formation of gums, sediment, and other deposits. Further insights into these degradation processes are provided in recent literature reviews on the topic [90,91]. Despite this importance, oxidative stability is not included in the tabular or graphical summaries of FAME properties in Table 9 and Fig. 4, respectively. The reason for this omission is that oxidative stability is determined not only by FAME compositional properties, but also by the age of the biodiesel and the conditions under which it has been stored. Furthermore, many biodiesel samples contain additives that improve stability without affecting the gross composition.

Oxidative stability is influenced by unsaturation. In general, higher unsaturation leads to poorer stability, although the autoxidation of unsaturated fatty compounds proceeds at different rates depending upon the number and position of the double bonds [90]. Oxidative degradation processes are initiated by extraction of a hydrogen atom from a carbon adjacent to a double bond – the so-called allylic position [53,92]. Following removal of this hydrogen, rapid reaction with molecular oxygen leads to formation of allylic hydroperoxides. Subsequent reactions involving isomerization and radical chain propagation produce numerous secondary oxidation products such as aldehydes, alcohols, and carboxylic acids. FAME molecules containing a carbon that is adjacent to two double bonds

(a bis-allylic group) are particularly susceptible to this type of oxidative instability. It is for this reason that the European biodiesel standard (EN 14214) includes a separate specification for linolenic acid methyl ester, which contains two bis-allylic groups (Table 2). When using purified methyl esters of oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3), the relative rates of autoxidation were measured to be 1:41:98 [93,94].

The importance of polyunsaturated FAME (as opposed to monounsaturated FAME) with respect to fuel stability has been recognized by many researchers. Ramos et al. defined a parameter called degree of unsaturation (DU), similar to the calculated "average unsaturation" property discussed above, but weighted di- and tri-unsaturated species twice as much as mono-unsaturated species [95]. Park et al. developed a predictive equation for biofuel stability that is based upon the concentrations of just two FAME species: linoleic FAME (18:2) and linolenic FAME (18:3) [96].

The relative amounts of saturated and unsaturated constituents shown in Fig. 3 are instructive in gauging the inherent oxidative stability of the biodiesel fuels produced from these feedstocks. For instance, very high oxidative stability would be expected for coconut-derived FAME, since it contains only about 2% polyunsaturated species (di- and tri- unsaturates). Biodiesel feedstocks having over 50% polyunsaturated FAME include camelina, corn, safflower, soy, and sunflower; thus, these would be expected to have poor inherent oxidative stability. Camelina-derived biodiesel is particularly noteworthy, as it contains about 35% tri-unsaturated FAME. Consequently, camelina biodiesel may be expected to have especially poor oxidative stability, though we are not aware of any reports of significant stability problems with this material.

The algal lipid profiles shown in Fig. 3 are strikingly different from the vegetable oil profiles. The significant levels of polyunsaturated constituents seen in many algal profiles certainly raise questions about the oxidative stability of biodiesel produced from these materials. This is an area requiring further investigation.

The carbon–carbon double bond orientation is important with respect to oxidative stability. Generally, the *trans* configuration is more stable than *cis* [94,97]. The practical impact of this is limited, however, as all natural fats and oils are dominated by *cis* configuration. Of greater practical value in improving biodiesel stability is the blending of two feedstocks having different levels of inherent oxidative stability. Reported examples of this include blending high stability palm FAME with poorer stability jatropha FAME [73] and soy FAME [98].

Another reliable method for improving biodiesel stability involves utilization of anti-oxidant additives [99,100]. Although raw fats and oils usually contain natural anti-oxidants such as tocopherols and carotenoids, synthetic anti-oxidants have generally been found to be more effective [91,101–104].

3.4. Optimal properties for biodiesel

As seen from the discussion above, changes in compositional features of FAME have significant impacts on the physical/chemical properties of biodiesel. Furthermore, changes in a single compositional feature (such as chain length, chain branching, and unsaturation) generally produce both desirable and undesirable changes in FAME properties. To a certain degree, this is unavoidable, as some properties have antagonistic relationships. For example, compositional features that favor good oxidative stability (high saturation and low unsaturation) lead to poor low temperature performance.

The most significant relationships between FAME compositions and properties are summarized graphically in Table 13. This table uses arrows of different thickness and length to characterize the changes in FAME properties resulting from an increase in value of each compositional feature. Long arrows indicate relatively large effects (likely to be noticeable to a perceptive user), while shorter arrows indicate relatively small effects. Thick arrows indicate relationships that seem certain, based upon consistency of literature reports, while narrow arrows are less certain. A "–" symbol indicates that the literature is inconsistent regarding this effect. A blank cell indicates that little (or no) literature information was found pertaining to this effect. It should be emphasized that Table 13 only represents the best judgment of this paper's authors, based upon their literature review and analyses of reported data.

Due to the conflicting impacts of certain FAME compositional features upon fuel properties, it is not possible to define a specific FA composition that is optimum with respect to all important properties. When considering properties that define the suitability of FAME as a fuel blendstock, those that are most important include cetane number, viscosity, cold flow, oxidative stability, and lubricity [105]. Of these five, the two properties that are generally regarded as most critical – and which vary the most with changes in biodiesel feedstock – are cold flow and oxidative stability.

Several researchers have investigated design of preferred FAME components to optimize biodiesel's performance with respect to cold flow and oxidative stability [95,106,107]. The consensus view is that an optimum composition would have relatively low levels of saturated FA (to minimize cold flow problems), low levels of poly-unsaturated FA (to minimize oxidative instability), and high levels of mono-unsaturated FA. Some have concluded that palmitoleic acid (16:1) and oleic acid (18:1) provide the best compromise between oxidative stability and cold flow, without excessive reduction of cetane number [105,106]. Efforts are underway in several laboratories to genetically modify the natural FA composition of vegetable oils (and algal lipids) to improve their suitability as biodiesel feedstocks [108–110]. Much of this work is focused on soybeans, with the goal of increasing oleic acid (18:1) and decreasing linoleic acid (18:2) and linolenic acid (18:3).

4. Regional fuel specifications and quality

4.1. Biodiesel standard specifications

One of the principal means of ensuring satisfactory in-use biodiesel fuel quality is establishment of a rigorous set of fuel specifications, such as ASTM D6751 (in the U.S.) and EN 14214 (in the European Union). Numerous other countries have defined their own standards, which in many cases are derived from either ASTM D6751 or EN 14214. Some countries have also worked together to define guidelines for regional biodiesel standards. For example, a group called the Asia-Pacific Economic Cooperation (APEC) issued a report in 2007 that addressed guidelines for standardizing biodiesel standards within the APEC region [111].

A detailed summary showing 17 different biodiesel standards pertaining to numerous countries around the world is provided in Supplemental Information Table S-1, along with the sources of information used to generate this table. In many countries, biodiesel standards are evolving, with modifications occurring frequently. Thus, some of these specifications may no longer be current. Also, some countries directly link their standards to ASTM D6751 or EN 14214, though it is not always clear whether updates to these standards occur automatically as the ASTM and EN standards change.

4.2. Quality control/quality assurance

Another means of ensuring satisfactory biodiesel product quality involves establishment and enforcement of quality control/quality assurance (QC/QA) programs. As early as 1999, the German Association for Quality Management of Biodiesel (abbreviated

Table 13
Typical relationships between FAME level/composition and fuel properties. Arrows indicate change in FAME properties resulting from increases in compositional items.[a]

FAME Composition \ FAME Properties	Viscosity	Density	CP, PP, CFPP	Cetane Number	Iodine Number	Heating Value, MJ/kg	Lubricity	Oxidative Stability
FAME Blend Level (from B0 to B20)	↑	↑	↑	↓↑	↑	↓	↑	↓
Average Chain Length	↑	-	↑	↑		↑		
Chain Branching			↓	↓				
Degree of Unsaturation	↓	↑	↓	↓	↑	↓	-	↓
Alcohol Length and Branching	↑		↓	-				

[a] *Notes*: Length of arrow indicates relative magnitude of effect.
Thickness of arrow indicates certainty/consistency of effect.
Symbol "–" indicates highly uncertain, or conflicting information.
Blank box indicates that no relevant information was found.
Impact of FAME blend level on Cetane Number depends upon the base fuel's CN.

AGQM in German) was established to deal with in-use fuel quality [112]. In the U.S., the National Biodiesel Board has addressed the issue of QC/QA by establishing the National Biodiesel Accreditation Commission that oversees and directs the BQ-9000 Quality Management System [113]. This Commission has issued three sets of requirements: one for biodiesel producers [114], one for biodiesel marketers [115], and one for biodiesel laboratories [116]. The BQ-9000 Program includes a combination of ASTM standards and a quality systems program that includes storage, sampling, testing, blending, shipping, distribution, and fuel management practices. By following these requirements, the company – not the fuel – receives accreditation.

4.3. In-use handling guidelines

Several organizations have defined in-use handling guidelines to help ensure satisfactory biodiesel quality in the marketplace. For example, NREL has issued a number of guidelines, with the latest edition being released in early 2009 [31]. More recently, CONCAWE issued a set of guidelines for handling and blending FAME in the European situation [32]. This report discusses the following major fuel quality concerns, and offers suggestions for mitigating each one:

- Stability and deposit formation.
- Cold temperature handling and operability.
- Solvency.
- Microbial contaminants.
- Water separation.
- Material compatibility.

4.4. Fuel quality surveys

Another aspect of ensuring overall product quality is application of in-use surveys. The first systematic field survey in the U.S. was conducted by NREL in 2004, who collected and analyzed 27 samples of B100 and 50 samples of B20 [117]. Results showed that 85% of the B100 samples met all ASTM D6751-03 standard specifications. However, it was noted that only 4 of the 27 samples would meet a minimum inhibition period of 3 h as measured by the Rancimat oxidation test. (The Rancimat test was not yet included in ASTM D6751 at the time of this study.) Similar problems with oxidative stability of the B20 samples were noted. This survey also highlighted blending problems in producing B20, as 18 of the 50 samples tested had biodiesel concentrations outside the accepted range of B18–B22 – with 7 being considerably higher and 11 being considerably lower than this range.

NREL conducted another nationwide fuel quality survey of B100 in 2006 [118]. Specification testing of 37 samples showed that 59% failed to meet the ASTM D6751 requirements applicable at this time. The main reasons for failures were excessive levels of total glycerine and low flash point. Such problems suggest insufficient quality control in the production and clean-up of FAME. These results were disturbing because they suggested a worsening of B100 quality between 2004 and 2006 survey periods. Oxidative stability was again pointed out as an area of concern. Although still not a standard specification at the time of this survey, the Rancimat test was conducted on 10 of the 37 B100 samples. Only 3 of these 10 had an induction period in excess of 3 h (the current specification).

The most recent nationwide B100 quality survey was conducted by NREL in 2007 [119]. In this case, all known biodiesel producers in the U.S. were approached, with 56 of the 107 producers supplying samples for testing and evaluation. These 56 samples were binned according to producer size, with 25 samples coming from small producers (<0.1 mg/y), 16 samples from medium-sized producers (0.1–1.0 mg/y) and 15 samples from large producers (>1.0 mg/y). Results from laboratory specification testing showed that the large producers nearly always met ASTM D6751 specifications. Biodiesel from small and medium-sized producers still had significant failures, with oxidative stability having the highest failure rate at 30%. (The Rancimat oxidative stability test was included in ASTM D6751 by this time.) It was also noted that B100 produced from used vegetable oils failed the specifications more often than B100 produced from other feedstocks. Based upon certain assumptions regarding production volumes, NREL concluded that 90% of B100 produced in the U.S. in 2007 met all specifications; a significant improvement over previous survey results. However, an important point to remember is that all B100 samples in the 2007 survey were voluntarily provided by willing producers. In the earlier surveys, samples were obtained from blenders and distributors, not from producers. This change in procedure could raise questions about sampling bias.

The 2004 biodiesel quality survey conducted by NREL included B20 samples, while the 2006 and 2007 surveys did not. Results from the 2004 survey raised questions about quality control in blending operations, as 36% of the samples had biodiesel contents outside the acceptable range of B18–B22. Other organizations have also highlighted concerns about blending problems. One study involving analysis of B20 obtained from retail fueling stations in 2007

showed that of the 19 samples tested, 8 were actually <B17, with 4 being <B5 [120]. This study also reinforced concerns about oxidative stability, as 45% of the samples failed to meet the Rancimat test specification. Very recently, NREL conducted a field quality survey of 40 biodiesel blends (mostly B6–B20) collected in the winter of 2009–2010 [121]. The results are encouraging, showing improved fuel quality compared to previous surveys.

Measurement of biodiesel blend concentrations has been an area of investigation for many years. Excellent reviews of analytical methods have been published recently [122,123]. Commonly used methods include chromatographic, spectroscopic, and wet chemical methods. However, many of these methods are expensive and time consuming. The new U.S. standard for B6–B20 blends (ASTM D7467-08) specifies use of method D7371, which utilizes mid-infrared spectroscopy [34]. Other spectroscopic methods utilizing near IR [124], UV [125], and visible light [126] have also been used with some success. Although not widely practiced, it appears possible to include an on-board vehicle fuel sensor for real-time determination of biodiesel content. It has been demonstrated that the same type of dielectric-based sensor used for gasoline/ethanol blends provides reasonably accurate measurements of biodiesel/diesel blends [127,128].

5. Summary and conclusions

Although the literature indicates considerable variability, there is growing consensus regarding the fatty acid (FA) profiles of vegetable oils and animal fats commonly used to produce fatty acid methyl esters (FAME). Clear differences in carbon chain length and degree of unsaturation are apparent from one feedstock to the next. These differences influence the properties and performance of biodiesel (FAME) and biodiesel blends. The compositional profiles of common vegetable oils are dominated by five fatty acid species: palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), and linolenic (18:3). Coconut oil is significantly different, containing large fractions of lighter fatty acid species – especially lauric (12:0) and myristic (14:0). Camelina is also somewhat different from most other vegetable oils, with linolenic acid (18:3) being its largest single constituent, along with smaller amounts of the heavier species, 20:1 and 22:1.

Compared to vegetable oils, relatively little detailed compositional information is available for algal lipids. FA compositional profiles have been determined for very few of the over 40,000 identified algal species. However, it is clear that compositional variability across different algal species can be extreme. Some species have much higher levels of unsaturation – and especially multi-unsaturation – than is typical for vegetable oils.

The physical and chemical properties of a biodiesel are determined by its chemical composition. Due to its considerable oxygen content (typically about 11%), biodiesel has lower carbon and hydrogen contents compared to petroleum diesel. This results in a reduction in mass energy content of about 10%, but a reduction in volumetric energy of only 5–7%. Two properties that greatly influence the overall behavior and suitability of FAME as a diesel blendstock are: (1) the size distribution of the fatty acid (FA) chains and (2) the degree of unsaturation within these FA chains. Variations in biodiesel produced from different feedstocks can be explained largely by these two properties.

The two most common sets of regulatory standards for biodiesel blendstocks are ASTM D6751 in the U.S. and EN 14214 in Europe. Some of the specifications comprising these standards are directly related to the chemical composition of the FAME – such as viscosity, cetane number, cloud point, distillation, and iodine value. Other specifications relate to the purity of the FAME product, and address issues pertaining to production processes, transport, and storage – such as flash point, methanol content, metals content, sulfur level, acid number, and cold soak filterability. Oxidative stability is an important property of biodiesel that is influenced by both FAME chemical composition and by storage and handling conditions. Fuel oxidation is related to unsaturation within the FA chain, and is especially promoted by multiple units of unsaturation. For this reason, the oxidative stability of camelina-based FAME and some algal-based FAME may be of concern.

Based upon an extensive review of published information, several important physical and chemical properties were compiled and compared for biodiesel fuels produced from 12 different vegetable oil and animal fat feedstocks. A computed fuel property, called "average unsaturation," was highly correlated with several other properties, including viscosity, specific gravity, low temperature performance metrics, cetane number, and iodine value. An increase in average unsaturation leads to lower cetane number and poorer oxidation stability, but improved low temperature performance. Another computed property, "average chain length," was not highly correlated with most other properties.

An increasingly recognized problem with some biodiesel fuels is their propensity to form insoluble precipitates upon storage at low temperature. In large part, this problem is believed to be due to the presence of trace impurities – particularly sterol glucosides and saturated monoglycerides. These same impurities impart favorable lubricity performance to biodiesel; thus efforts to eliminate them could have an unintended consequence of worsening lubricity.

Due to the conflicting effects certain FAME compositional features upon different fuel properties, it is not possible to define a single composition that is optimum with respect to all important properties. However, useful formulation guidelines can be offered with respect to two critical biodiesel fuel properties: (1) low temperature performance and (2) oxidative stability. For good low temperature performance, biodiesel should have low concentrations of long-chain saturated FAME. For good oxidative stability, biodiesel should have high concentrations of saturated and mono-unsaturated FAME, but low concentrations of multi-unsaturated FAME.

Acknowledgements

This work was conducted under sponsorship and funding of the Coordinating Research Council (CRC). The authors gratefully acknowledge the CRC AVFL-17a Panel for their helpful guidance and suggestions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.rser.2011.07.143.

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